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Hazardous Waste Disposal Program, Sixth Monthly Report

TRW Systems Group

Prepared For
Environmental Protection Agency

July 10, 1972

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The program is divided into six major tasks consisting of: Defining Adequate Waste Management; Evaluating Presently Employed Waste Management Techniques or Policies and Making Recommendations as to Adequacy; Performing Field Surveys and Verification Experiments on Existing Management procedures; Defining, Planning and Outlining Research Programs Where Necessary for Elimination of Hazards; Conducting Proof-of-Principle Experimentation on the Most Promising Concepts; and Correlating Total Program Effort. During the last month first draft profile reports for 45 compounds were completed. 37 compounds were scheduled. The reports completed during June are as follows: Ammonium Fluoride, Ammonium Bifluoride, Sodium Fluoride, Sodium Bifluoride, Potassium Fluoride, Potassium Bifluoride; Antimony Pentafluoride and Antimony Trifluoride; Barium Compounds: Barium Carbonate, Barium Chloride, Barium Cyamide, Barium Nitrate, Barium Sulfide; Benzyl Chloride; Diborane, Tetraborane, Pentaborane-9, Pentaborane-11, Hexaborane, Decarborane; Calcium Arsenite, Copper Aceloarsenite, Lead Arsenite, Potassium Arsenite, Zinc Arsenite; Chloropicrin; Chrome; Chromic Acid; 2,4-D; Dinitro Cresol; Ethylene Bromide, Methyl Bromide, Methyl Chloride; Hydrazine; Hydrocyanic Acid, Hydrogen Cyanide; Mercuric Cyanide; Nitrochlorobenzene; Nitrogen Mustards; Sodium Azide; Tetraethyl and tetramethyl lead.

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Pesticides
Cyanides
Storage
Transportation

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HAZARDOUS WASTE DISPOSAL PROGRAM

SIXTH MONTHLY REPORT

CONTRACT 68-03-0089

Prepared for
the
Environmental Protection Agency

10 July 1972

TRW
SYSTEMS GROUP
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

HAZARDOUS WASTE DISPOSAL PROGRAM

SIXTH MONTHLY REPORT

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1. INTRODUCTION

Under the requirements of Section 212 of Public Law 91-512, The Office of Solid Waste Programs of the Environmental Protection Agency is in part required to prepare "a comprehensive report and plan for the creation of a system of national disposal sites for the storage and disposal of hazardous wastes, including radioactive, toxic chemical, biological, and other wastes which may endanger public health or welfare. Such a report shall include: 1) a list of materials which should be subject to disposal in any such site; 2) current methods of disposal of such materials; 3) recommended methods of reduction, neutralization, recovery, or disposal of such materials.

Contract 68-03-0089 is the second in a series of EPA projects which are designed to provide the information required in the report to Congress. The principle objective of the current program is to define and evaluate the waste management techniques and policies currently utilized for a specified set of hazardous wastes. Waste management techniques which will be evaluated include those for storage, handling, transport, neutralization, detoxification, reuse, and disposal. Other aspects of the program include description of possible new techniques for management of hazardous wastes, proof-of-principal experimentation to determine the effectiveness of techniques for which insufficient data is available for adequate evaluation, and planning of research programs necessary for developing new procedures and processes for treating hazardous wastes for which adequate techniques do not currently exist.

This sixth monthly technical report summarizes the work performed by TRW for EPA from June 1, 1972 to June 30, 1972 under Contract 68-03-0089.

2. PROGRAM ACCOMPLISHMENTS

The program is divided into six major tasks consisting of:

- Defining Adequate Waste Management. Toxicity information and toxicological standards on each hazardous material contained in lists supplied by the Solid Waste Research Office will be reviewed. Other factors (such as flammability or explosive potential) which affect the waste management process will be investigated where applicable. Acceptable criteria in terms of impact on mankind and the environment for each of the waste management steps (handling, storage, transportation, disposal, etc.) shall be defined.

- Evaluating Presently Employed Waste Management Techniques or Policies and Making Recommendations as to Adequacy. The existing techniques for waste management of each hazardous material (supplied as in Task 1) will be assessed in relation to the criteria defined in the first task. Adequate techniques shall be recommended in order of preference and any required state-of-the-art modifications prescribed. Techniques which are applicable to national disposal sites will be specified.

- Performing Field Surveys and Verification Experiments on Existing Management Procedures. In cases where adequate information to determine the effectiveness of a particular waste management technique are not available, special field surveys or verification experiments will be performed. Results of those studies will be recycled to Task 2 to complete the evaluation of the particular hazardous waste material.

- Defining, Planning and Outlining Research Programs Where Necessary for Elimination of Hazards. Where no acceptable waste management techniques currently exist for a particular hazardous waste material, efforts will be made to innovate new approaches and the necessary research and/or demonstration programs will be planned and outlined. Prioritization of the programs in terms of importance of the problem and probability of success will be accomplished.

- Conducting Proof-of-Principle Experimentation on the Most Promising Concepts. Within the constraints of schedule and budget, proof-of-principle type experimentation will be conducted on the most promising but unproven concepts.

- Correlating Total Program Effort. The program is directed to provide inputs to a final report which will: 1) summarize the best available waste management techniques for each material; 2) list on a prioritized basis those techniques to be included at possible National Disposal Sites; and 3) indicate major gaps in current hazardous waste management technology and provide a comprehensive, prioritized research and development plan for obtaining the required technology.

During June effort was concentrated primarily on Tasks 1, 2 and 5 of the program. The specific areas addressed were: 1) Treatment Process Reports; 2) Profile Reports; and 3) Identification of Research Needs. These efforts are discussed in the following sections.

2.1 TREATMENT PROCESS REPORTS

The scheduled preparation of detailed reports describing the most important and frequently used techniques for the disposal or recovery of hazardous waste materials was completed during June. The report on Pyrolysis was prepared during the last month in first draft form and is presented in Appendix A for review. Although not previously scheduled, brief descriptions of various exhaust gas cleaning devices will be prepared during July to provide more complete background for the incineration processes and other processes with which they are normally found.

2.2 PROFILE REPORT

During the last month first draft profile reports for 45 compounds were completed. 37 compounds were scheduled. The reports completed during June are listed below and are presented in Appendix B.

Hazardous Material Number	Hazardous Material Name
23,346,389	Ammonium Fluoride, Ammonium Bifluoride, Potassium Fluoride, Potassium Bifluoride, Sodium Fluoride, Sodium Bifluoride
36,43	Antimony Pentafluoride and Antimony Trifluoride
52,53,469,471,472	Barium Compounds: Barium Carbonate, Barium Chloride, Barium Cyamide, Barium Nitrate, Barium Sulfide

Hazardous Material Number	Hazardous Material Name
58	Benzyl Chloride
61,505	Diborane, Tetraborane, Pentaborane-9, Pentaborane-11, Hexaborane,Decarborane
88,377,490,236,341,454	Calcium Arsenite, Copper Aceloarsenite, Lead Arsenite, Potassium Arsenite, Zinc Arsenite
111	Chloropicrin
113	Chrome
114	Chromic Acid
135	2,4-D
162	Dinitro Cresol
182,267,268	Ethylene Bromide, Methyl Bromide, Methyl Chloride
212	Hydrazine
215,218	Hydrocyanic Acid, Hydrogen Cyanide
254	Mercuric Cyanide
302	meta and para Nitrochlorobenzene
306	Nitrogen Mustards: HN-1, HN-2, and HN-3
378	Sodium Azide
425,427	Tetraethyl and tetramethyl lead

2.3 IDENTIFICATION OF RESEARCH NEEDS

The proof-of-principle experimentation to be performed under the TRW funding of Task V is designed to determine the feasibility of new concepts for waste treatment or recovery processes. The approach proposed by TRW for selecting concepts to be tested requires; first, the identification of areas where technology gaps exist and where research is needed; second, the proposal of specific projects of sufficient promise and scoped in cost and time to be completed within the constraints of the program; and third, the specific approval of the project monitor. During June the general areas where currently identified technology gaps exist were examined to determine possible research needs amenable to proof-of-principle testing.

The general technology gaps identified to date fall into two categories: areas where information necessary to a complete understanding is lacking and areas where technology for adequate treatment either is totally lacking or is untried. The gaps identified in the current program are listed below by areas.

Toxicology

Under this program Hazleton Laboratories currently is providing estimated acceptable limits for hazardous materials in air, water, and soil environments. These values are based on literature information including threshold limit values for occupational exposure, fish toxicity, and animal test data. Much of the information necessary for accurate estimation is not available from these sources and direct research on the hazardous materials with aquatic and terrestrial animals is requred.

Ocean Disposal

Information on the effects of many of the materials on the ocean environment is lacking as was pointed out in the ocean disposal description in the Fifth Monthly Report. The potential harm associated with many materials is unknown and requires research to define the fates of the materials in the ocean.

Landfill Disposal

Much of the information necessary to the quantitative determination of the suitability of landfill disposal for specific hazardous wastes has not been determined. As was mentioned earlier toxicity information from which human toxicity and groundwater toxicity can be determined are often unavailable. The biodegradability of many of the materials considered in this program are unknown. The mobility of the waste (ease with which it moves through landfills) is also unknown for many materials. The technology for stabilizing hazardous materials in a landfill environment requires research and development both to provide information on its possible utility and to improve its effectiveness.

Land Burial (Permenant Storage)

The interest in this procedure, based on the requirement for permanent storage of radioactive wastes, has led to much research on the suitability of various types of land burial techniques. The availability of container materials appropriate to isolating the wastes (radioactive or toxic) from the storage environment is an area where apparently both further information related to the surviability of currently available materials and further development directed at increasing surviability is required.

Biological Treatment

Here again the data base on the biodegradability of specific waste materials requires further research. Data on the long-term effects of many materials in the environment (e.g., chronic plant toxicology) are also unknown.

Recognizing the requirements outlined above, a set of proposals describing specific proof-of-principal test programs have been prepared and will be reviewed by the project monitor in a meeting scheduled for early in July at TRW.

3. WORK PLANNED FOR JULY

The Profile Report preparation will continue as scheduled. As was mentioned earlier, the treatment process descriptions will be expanded to include gas cleaning devices commonly associated with processes, such as incineration. The additional effort proposed by TRW for determining the forms in which various hazardous wastes are found, their quantities and their locations was funded at the end of June and this effort will be initiated in July.

APPENDIX A - PROCESS EVALUATION REPORT

PYROLYSIS

1. INTRODUCTION

Pyrolysis is generally defined as the thermal decomposition of a compound. With respect to waste carbonaceous materials, pyrolysis represents a means of converting the unwanted waste into a usable commodity with economic value. That is, most municipal and industrial wastes which are basically organic in nature can be converted to coke or activated charcoal and gaseous mixtures which may approach natural gas in heating values through the utilization of pyrolysis.[1011, 1433]

Pyrolysis has only recently (1968) been applied to the conversion of organic wastes. The process has traditionally been used to convert low economic value homogeneous materials, such as wood chips and heavy hydrocarbon still bottoms, to compounds with higher overall economic value, such as fuel gas, pitch, creosote, acetic acid, crude methanol and charcoal (as in the case with wood chips), and coke, fuel gas and gas oil (as in the case with still bottoms).[1433,1662] For purposes of this report, only the methods associated with waste conversion will be discussed.

2. OPERATION PRINCIPLE[0145,1009]

The heart of the pyrolytic waste conversion process is the pyrolytic converter (Figure 1). The unit consists of a sealed, airtight retort cylinder inside a heavy insulating jacket. The gas-fired retort revolves slowly on a slight decline from infeed to outfeed. Wastes are injected through a seal area that intermittently opens (the flapper valve seal is designed to minimize entry of oxygen).

Inside the retort, ground-up wastes are subjected to temperatures of about 1200 F - plus or minus 300 F, depending upon the nature of the wastes, in an essentially oxygen-free atmosphere. Without oxygen, the wastes cannot burn and are broken down (pyrolyzed) into steam, carbon oxides, volatile vapors and charcoal.

Steam, carbon dioxide and carbon monoxide are the first gases to emerge. They are trapped and then: (1) vented after flaring; (2) used to dry incoming feed; or (3) the steam can be condensed and the effluent gas burned for fuel value.

As the wastes are heated further, volatile gases are distilled. Typically, these gases will include hydrogen, methane, ethylene and ethane. About 25 cubic feet of combustible gases are recovered from every pound of industrial and municipal refuse. Energy value per cubic foot is usually between 400 and 500 Btu.

The crude, combustible gas is drawn off and used in part (30 to 40 percent) to fuel the converter while the remainder may be utilized to fuel other equipment or to make steam for such uses as heating and power generation.

In fact, a 100-ton per day municipal waste conversion facility will produce enough excess gas to create 400,000 kilowatts of electricity per day. At a quarter-cent per KW, that amounts to $1000 of electrical energy per day. Thus, recovery of combustible gas usually offsets the total operating costs of a waste-conversion facility.

The surplus gas cannot be piped over any great distance and retain its original heat value. Nor can it be stored. For, allowed to cool, pyroligneous acids begin to condense, reducing heat value per cubic foot to around 350 Btu and reducing volume by as much as 80 percent.

However, the liquid condensate is of economic value. It constitutes a form of cresotar which is used for, among other things, dust control on unpaved roads. Moreover, the liquid represents a potentially valuable source of organic compounds. Chemical analyses have identified such constituents as methanol, ethanol, isobutanol, n-pentanol, tert. pentanol, 1,3-propanedial, 1-hexanol, acetic acid and various other alcohols, ketones and tars.

The last by-product is charcoal. Generally 30 to 35 percent of input by weight is recovered in this form, and each pound of charcoal has an approximate heat value of 12,000 Btu. Used as fuel, it can create about half the electricity expected from the recovered gas.

Other major pieces of equipment required for a municipal or industrial waste-conversion facility are a hogger/grinder, a magnetic separator, conveyors, and storage facilities. A hogger/grinder is necessary because converters generally operate best when solid waste materials are reduced to no more than a few inches in size. Since pyrolysis units do not usually vent any products to the atmosphere, they do not require any air pollution control equipment.

3. PROCESS DESIGN[0145, 1009]

Pyrolytic conversion processes are generally custom-engineered according to input volumes and types of waste being treated. For this reason, there is not a great deal of specific design information available. Converters have been made with capacities ranging from 1/4 ton to 12 tons per hour. Units can be installed in batteries to handle more than 12 tons per hour. For instance, one municipal pyrolytic process utilizes four 4-ton per hour converters.

Intake-to-discharge cycles vary with heat intensity, the converters length, and its rotational speed. The average for industrial and municipal refuse is 12 to 15 minutes. Such hard to pyrolyze materials as coal (which is converted into coke) and rubber may take as long as 30 minutes.

Operational temperatures will vary with waste type and desired products. Operating temperatures are usually in the 1200 F ± 300 F range with the lower operating temperature generally resulting in greater residue (coke), tar and light oil yields and lower gas yields (Tables 1 and 2).

4. PROCESS ECONOMICS[0582, 1010]

The primary factors determining the capital cost of pyrolysis systems include waste flow rate, waste composition, secondary effluent treatment for product recovery, and materials of construction. Operating costs are determined by labor rates, maintenance requirements, and conversion product values.

An exhaustive economic analysis of a commercial size (5,000 tons/day) municipal refuse pyrolysis plant was made in 1970 by Cities Service Oil Company.[1010] The study indicated that a total investment including working capital) of 32.6 million dollars was required and that the associated operating cost would be \$2.14 per ton of refuse pyrolyzed (Table 3). There is no economic data available with respect to industrial waste pyrolysis processes.

5. PROCESS MODIFICATIONS[0582,1010]

Modifications to the pyrolysis process generally involve treatment of converter effluents (Figure 2). The pyrolysis oils may be sent through a hydrotreating unit and converted to industrial fuel oil. The pyrolysis effluent gas may be cooled and the resultant condensate separated into its components, namely acetic acid, methanol, furfural, acetone, butyric acid, propionic acid, methyl ethyl ketone, light fuel oil, and other water soluble volatile organics, through the use of conventional separation techniques. The cooled wet gas may be dried and utilized as fuel gas. The char-like pyrolysis residue can be further treated and converted into activated carbon.

6. PROCESS APPLICABILITY

The utilization of pyrolytic processes to convert waste into useful materials is a relatively new concept. For this reason, there are few processes in operation today. Those processes which are in operation convert municipal refuse, industrial refuse, paint sludges, tires, plastics and other organic polymers into materials with economic value.[1009,1011]

Although the pyrolytic converter is a versatile piece of equipment that can be operated under varying conditions with various feed materials, its auxiliary equipment tends to be specific for various feeds and desired end products. For that reason, the overall pyrolytic process tends to lack versatility.

At a National Disposal Site, a pyrolysis unit would probably find little direct application as a hazardous waste conversion unit. However, if sufficient refuse was generated at the site, a pyrolysis unit could be utilized to convert it into fuel gas for use in other operations (furnaces, incinerators, reboilers, boilers for steam production and possible subsequent conversion to electricity, etc.) and coke which could be utilized for its heat content or converted to activated carbon for use in water treatment facilities.

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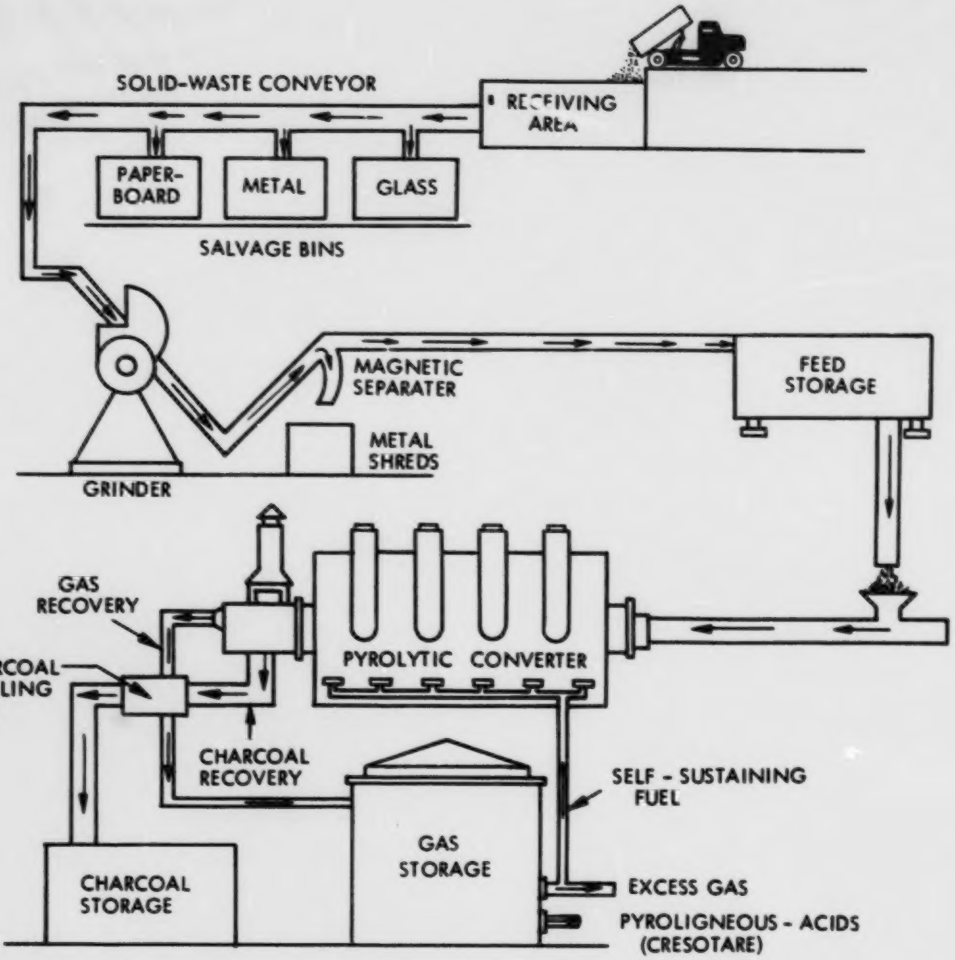
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RECEIVING AREA
PAPER-BOARD
METAL
GLASS
SALVAGE BINS
MAGNETIC SEPARATER
FEED STORAGE
METAL SHREDS
GRINDER
GAS RECOVERY
CHARCOAL COOLING UNIT
PYROLYTIC CONVERTER
CHARCOAL RECOVERY
SELF - SUSTAINING FUEL
GAS STORAGE
CHARCOAL STORAGE
EXCESS GAS
PYROLIGNEOUS - ACIDS (CRESOTARE)

Figure 1. Pyrolytic waste conversion[1009]

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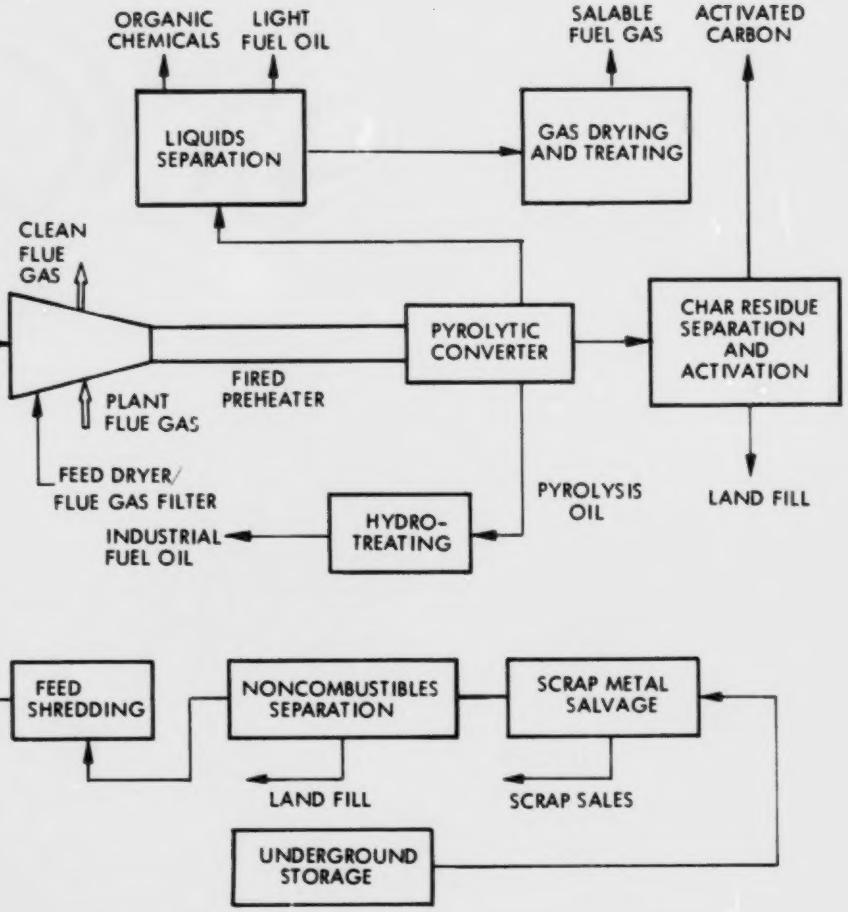
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LIGHT FUEL OIL
SALABLE FUEL GAS
ACTIVATED CARBON
LIQUIDS SEPARATION
GAS DRYING AND TREATING
CLEAN FLUE GAS
PYROLYTIC CONVERTER
CHAR RESIDUE SEPARATION AND ACTIVATION
FIRED PREHEATER
PLANT FLUE GAS
FEED DRYER/ FLUE GAS FILTER
PYROLYSIS OIL
LAND FILL
INDUSTRIAL FUEL OIL
HYDRO-TREATING
FEED SHREDDING
NONCOMBUSTIBLES SEPARATION
SCRAP METAL SALVAGE
LAND FILL
SCRAP SALES
UNDERGROUND STORAGE

Figure 2. Secondary treatment alternatives

TABLE 1. YIELDS OF PRODUCTS FROM PYROLYSIS OF MUNICIPAL AND INDUSTRIAL REFUSE[0145]

Refuse	Pyrolysis temp, F	Yields, weight-percent of refuse							Yields per ton of refuse				
		Residue	Gas	Tar	Light oil in gas	Free ammonia	Liquor	Total	Gas, cubic feet	Tar, gallons	Light oil in gas, gallons	Liquor, gallons	Ammonium sulfate, pounds
Raw municipal	930-1650	9.3	26.7	2.2	0.5	0.05	55.8	94.6	11,509	4.8	1.5	133.4	17.9
	1380	11.5	23.7	1.2	.9	.03	55.0	92.3	9,628	2.6	2.5	131.6	23.7
	1650	7.7	39.5	.2	-	.03	47.8	95.2	17,741	.5	-	113.9	25.1
Processed municipal containing plastic film	930-1650	21.2	27.7	2.3	1.3	.05	40.6	93.2	11,545	5.6	3.7	96.7	16.2
	1380	19.5	18.3	1.0	.9	.02	51.5	91.2	7,380	2.2	2.6	122.6	28.4
	1650	19.1	40.1	.6	.2	.04	35.3	95.3	18,058	1.4	.6	97.4	31.5
Industrial-Sample A	930-1650	36.1	23.7	1.9	.5	.05	31.6	93.9	9,563	4.1	1.4	75.2	12.5
	1380	37.5	22.8	.7	.9	.03	30.6	92.5	9,760	1.5	2.6	73.0	19.5
	1650	38.8	29.4	.2	.6	.04	21.8	90.8	12,318	.5	1.6	51.1	21.7
Industrial-Sample B	930-1650	41.9	21.8	.8	.6	.03	29.5	94.6	9,270	1.7	1.6	70.2	20.4
	1380	31.4	25.5	.8	.8	.03	31.5	90.0	10,952	1.8	2.2	74.9	21.2
	1650	30.9	31.5	.1	.5	.03	29.0	92.0	14,065	.02	1.4	68.5	22.9

TABLE 2. CHEMICAL ANALYSES*OF SOLID RESIDUES FROM PYROLYSIS OF MUNICIPAL AND INDUSTRIAL REFUSE[0145]

Refuse	Pyrolysis temp, F	Proximate, percent				Ultimate, percent					Heating value, Btu/lb	Heating value, million Btu/ton
		Moisture	Volatile matter	Fixed carbon	Ash	Hydrogen	Carbon	Nitrogen	Oxygen	Sulfur		
Raw municipal	930-1650	2.6	4.4	29.6	66.0	0.4	32.4	0.5	0.5	0.2	5,020	10.040
	1380	2.2	7.4	51.4	41.2	.8	54.9	1.1	1.8	.2	8,020	16.040
	1650	1.0	4.7	31.7	63.6	.3	36.1	.5	.0	.2	5,260	10.520
Processed municipal containing plastic film	930-1650	1.7	4.8	56.7	38.5	.6	57.7	.8	2.1	.3	8,800	17.700
	1380	1.3	13.4	34.6	52.0	.8	41.9	.8	4.4	.1	6,080	12.160
	1650	1.2	3.3	53.5	43.2	.5	53.4	.7	1.8	.4	8,090	16.180
Industrial - Sample A	930-1650	.9	2.6	15.2	82.2	.3	17.0	.1	.2	.2	2,520	5.040
	1380	1.2	5.1	17.0	77.9	.5	19.4	.2	1.8	.2	2,900	5.800
	1650	.1	2.5	12.9	84.6	.3	14.8	.2	.0	.2	2,180	4.360
Industrial - Sample B	930-1650	.3	3.0	9.7	87.3	.2	11.8	.1	.4	.2	1,660	3.320
	1380	1.0	3.6	16.6	79.8	.3	19.5	.2	.0	.2	2,680	5.360
	1650	.2	6.4	16.2	77.4	.4	19.3	.3	2.4	.2	2,810	5.620

*Moisture on as-received basis; all other data on dry basis.

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TABLE 3. INVESTMENT AND OPERATING COSTS FOR A 5000 TON/DAY MUNICIPAL PYROLYSIS PLANT[1010]

Capital Investment

Investment	$ Million
Inside battery limits	16.0
Offsites	6.4
Total	22.4
Additional Costs	
Contingency (25%)	5.6
Construction interest, first year (8% x 33%)	0.7
Construction interest, second year (8% x 67%)	1.5
Startup extraordinary (assumed 8% x 100%)	2.4
Total additional costs	10.2
Total investment (includes working capital)	32.6

Operating Costs

Fixed Costs	$ Million (per year)	
Labor	0.49	
Supervision	0.15	
Overhead	0.64	
Maintenance, onsite	1.00	
Maintenance, offsite	0.24	
Taxes and Insurance	0.49	
Total fixed costs	3.01	$1.65/ton
Variable Costs		
Water and power	0.20	
Fuel	0.70	
Total Variable Costs	0.90	$0.49/ton
Total Operating Costs	3.91	$2.14/ton

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APPENDIX B - PROFILE REPORTS

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PROFILE REPORTS ON THE ALKALI AND AMMONIUM FLUORIDES

Ammonium Fluoride (23), Ammonium Bifluoride, Potassium Fluoride (346), Potassium Bifluoride, Sodium Fluoride (389), Sodium Bifluoride

I. GENERAL

Introduction

The alkali and ammonium fluorides are similar in their chemistry, toxicology, and other hazards. Because of this, ammonium fluoride, ammonium bifluoride, potassium fluoride, potassium bifluoride, sodium fluoride, and sodium bifluoride are included in a combined profile report.

Ammonium Fluoride

Ammonium fluoride is a colorless, crystalline deliquescent solid, supplied commercially as a granular powder.[1492] The salt decomposes on heating,[1433] and corrodes glass.[1492] The physical and chemical properties of NH_4F are summarized in the attached worksheet.

The salt is prepared by the reaction of anhydrous ammonia and ice-cold 40 percent hydrofluoric acid:[1492]

$$NH_3 + HF \rightarrow NH_4F$$

The major uses of ammonium fluoride are:

1. Etching and frosting glass
2. As antiseptic in brewing beer
3. As mothproofing agent
4. In preserving wood

5. In printing and dyeing textiles.

Ammonium fluoride has been suggested as an intermediate in the manufacture of acid-grade CaF_2 (fluorspar) from by-product fluosilicic acid produced in very large quantities by the wet phosphoric acid process.[0148] The proposed reactions, which have been investigated on a laboratory and pilot scale are:

$$H_2SiF_6 + 6\ NH_3 + 2\ H_2O \rightarrow SiO_2\downarrow + 6\ NH_4F$$

$$Ca(OH)_2 + 2\ NH_4F \xrightarrow{\Delta} CaF_2\downarrow + 2\ NH_3\uparrow + 2\ H_2O$$

Ammonium Bifluoride

Ammonium bifluoride is a white, crystalline, transparent solid. Solutions of the salt are acid, and the dry crystals have an acid odor. The commercial product is marketed in flake form, and is hygroscopic at humidities above 50 percent. Ammonium bifluoride corrodes glass readily; it should be stored in a tightly closed plastic, rubber, wood or parafinned container. The attached worksheet contains a summary of physical and chemical properties.

Ammonium bifluoride is prepared on a large scale by reacting anhydrous ammonia and anhydrous HF:[1433]

$$NH_3 + 2\ HF \rightarrow NH_4\ HF_2$$

The gases are injected into a cooled, packed tower, and the resultant liquid $NH_4\ HF_2$ is flaked on a cooled rotary drum. An alternative process, used for the production of crystalline $NH_4\ HF_2$, is the batch reaction of ammonium hydroxide solution with aqueous hydrofluoric acid, followed by evaporation, cooling, crystallization, and centrifugation. The mother liquor from the crystallization is recycled to the evaporation step of the process with the next batch of dilute $NH_4\ HF_2$ solution.

The major uses of ammonium bifluoride are:

1. In combination with hydrofluoric acid, as a commercial glass frosting and etching agent.
2. As a laundry sour, because of its capability to decolorize iron stains.
3. In the removal of silica scale from steam boilers and automotive radiators.
4. In the manufacture of magnesium and magnesium alloys.
5. In brightening aluminum.
6. In oil well treatment.
7. In washing glass television tube blanks and faceplates, greenhouses, and factory windows.
8. As a fungicide, in treating wood.
9. In breweries and distilleries.

Potassium Fluoride

Potassium fluoride is a white, transparent, hygroscopic crystalline powder, available commercially as either the anhydrous salt, or the dihydrate. Two hydrates are known - $KF.2H_2O$, and $KF.4H_2O$. The salt is very freely soluble in boiling water.[1492] The anhydrous salt may be stored in aluminum containers. Aqueous solutions of KF corrode glass and porcelain. The physical and chemical properties are summarized in the attached worksheet.

Potassium fluoride is prepared commercially by reacting potassium carbonate with aqueous hydrofluoric acid. Extreme care is necessary in judging the neutralization point, since in concentrated solutions both potassium bifluoride and potassium bicarbonate are stable in the presence of the other. The resultant neutral solution is concentrated and cooled. The anhydrous salt is obtained by arresting the cooling at 50-55 C and removing the crystals by centrifuging at this temperature.

If the dihydrate is desired, the solution is cooled to room temperature and the resulting crystals are centrifuged and packaged as moist crystal. The anhydrous salt is also prepared in flake form by passing the hot concentrated solution over a heated rotary drum dryer. Extreme care is necessary in handling the anhydrous salt to prevent rehydration.

The major uses of KF are:

1. In the fluorination of organic compounds
2. In flux for hard solder (silver solder)
3. To prevent fermentation
4. In insecticide formulations
5. For frosting glass
6. As a solvent, in preparing barium titanate crystals
7. As a fire extinguisher in alkali metal fires

Potassium Bifluoride

Potassium bifluoride is a white, crystalline salt, which assumes one of two solid forms, dependent upon temperature. Between 194 and 239 C, the β-form--a soft white solid--is the stable phase. At 195 C, the β-form changes to the α-form, a hard white solid, stable below 195 C.

Potassium bifluoride is manufactured commercially from potassium carbonate and hydrofluoric acid. A slight excess of HF over the stoichiometric amount is used. The solution is concentrated to a specific gravity of 45 Baume and cooled to form the crystals. The crystals are separated by centrifugation, dried, ground and packaged in polyethylene-lined fiber drums containing 100 or 400 lbs.[1433] The commercial salt contains about 0.5 percent KF.

The major uses of KHF_2 are:

1. As an electrolyte, in conjunction with HF, in the preparation of F_2.
2. As the basis for most silver soldering fluxes.

3. In frosting glass.
4. In the preparation of pure anhydrous HF in the laboratory.
5. As a co-catalyst, with BF_3, in the alkylation of benzene with olefins.[1433]

Sodium Fluoride

Sodium fluoride is a white crystalline powder, available commercially in three grades--90, 95 and 98 per cent purity-- and two densities--light (37 cubic in./lb), and dense (23 cubic in./lb). Aqueous solutions are alkaline, and etch glass.

Sodium fluoride is manufactured commercially by reacting soda ash with 40 percent hydrofluoric acid.

$$Na_2CO_3 + 2\ HF \rightarrow 2NaF + H_2O + CO_2\uparrow$$

The crystals precipitate immediately,[1492] are separated and dewatered, dried, sized and packaged.[1433] The reactors are usually rubber or carbon brick-lined steel. Process piping is rubber hose, stainless steel, or plastic-lined steel. Valves are rubber or plastic-lined diaphragm valves, or plastic-lined plug cocks[1433].

The commercial material is packaged in 100 lb multiwall bags and 125 and 400 lb fiber drums. Sodium fluoride for insecticidal purposes must be colored blue. Some states require that the word "Poison", together with information on appropriate antidotes, appear on the labels of the packages. Sodium fluoride shipped in interstate commerce must carry a Manufacturing Chemists Association (MCA) warning label.

The major uses of sodium fluoride are:

1. As insecticide.
2. In other pesticide formulations.

3. In the fluoridation of water.
4. In soldering and metallurgical fluxes.
5. In the manufacture of rimmed steel.
6. In electroplating.
7. As a constituent of vitreous enamel and opal glass mixes.
8. In heat treating salts.
9. For pickling stainless steel.
10. As a disinfectant in breweries and distilleries.
11. As a glue and paste adhesive preservative.
12. In the manufacture of coated papers.

Sodium fluoride solution is applied topically to the teeth as a 2 percent solution, for prevention of dental cavities.[1492] Sodium fluoride has been responsible for more lethal and acute cases of fluoride poisoning than all other fluorides combined.[1988]

Sodium Bifluoride

Sodium bifluoride is a white, free-flowing granular material supplied at a commercial purity of about 99 percent. The material has limited solubility in water, and decomposes into NaF and HF above 150 C. The attached worksheet summarizes the chemical and physical properties of sodium bifluoride.

$NaHF_2$ is made by reacting soda ash or caustic soda with hydrofluoric acid. An adequate concentration of excess HF is maintained, in order to crystallize the bifluoride. The slurry is dewatered, dried, screened and packaged. Spray drying has been used to some extent. Cooling of the reaction is necessary to avoid self-heating to an undesirably high temperature. The reactors are usually rubber- or carbon brick-lined steel. Process piping is rubber hose, stainless, or plastic-lined steel, with rubber or plastic-lined diaphragm valves or plastic-lined plug cocks.

Sodium bifluoride is available in 100 lb multiwall bags and 125, 375 and 400 lb fiber drums. The salt hydrolyzes readily, and can cause hydrofluoric acid burns to the skin.

Major uses of sodium bifluoride are:

1. As a laundry sour and stain remover.
2. In bleaching leather and treating hides.
3. In plating tin.
4. Etching and frosting glass.
5. Cleaning stone and brick building faces.

2. TOXICOLOGY

Human Toxicity

The use of the fluorides as insecticides and rodenticides is so widespread that sodium fluoride is almost a common household preparation. Because of the innocuous appearance of sodium fluoride prior to the law requiring that it be colored blue, the white powder was easily mistaken for powdered milk, baking powder, powdered sugar, corn starch, or pancake flour. This, coupled with the custom of keeping insecticides in the cupboard along with soaps and washing powders, produced many tragic cases of fluoride poisoning.[1988]

The alkali and ammonium fluorides, like the other soluble fluorides can cause both acute and chronic poisoning. Fatal human poisonings generally have taken place after the ingestion, accidentally or by suicidal intent, of a large quantity (5 to 10 grams) of sodium fluoride. The course is violent and brief, with death occurring within two to four hours. The symptoms of acute fluoride poisoning include extreme nausea and vomiting, perspiration, salivation, burning, cramp-like abdominal pains, diarrhea, dehydration and thirst, muscle weakness; hemorrhagic gastroenteritis, muscle weakness, central nervous depression, cyanosis, shock, weak and thready pulse, shallow unlabored respiration, weak heart tones, paralysis of the muscles of deglutation, carpopedal spasm, spasm of the extremities, and, in extreme cases, death.[1988] Lethal dosages of 1-1/2 to 2 grams (25 to 30 grains) expressed as F, of soluble fluorides have been reported.[1988] Prompt treatment has averted death in one case where 50 to 80 grams of NaF was ingested.[1988] Severe illness can follow ingestion of as little as 66 mg (about 1 grain) of F.

Fluoride kills by a blockade of the normal metabolism of the cells, inhibiting the enzymes involved in essential processes. Vital functions--e.g., the origin and transmission of nerve impulses--cease. Necessary bodily functions controlled by calcium, such as blood clotting and membrane permeability, are interfered with. Cell damage and necrosis produce massive impairment in the function of vital organs. There is a characteristic shock-like syndrome terminally.[1988]

Treatment of acute fluoride poisoning emphasizes intravenous and intramuscular injections of 10 percent calcium gluconate solution, intravenous injection of glucose in isotonic saline, gastric lavage with lime-water or 1 percent $CaCl_2$ solution, treatment for shock and dehydration, and the absolute necessity for quick response.

The bifluorides hydrolyze, and cause hydrofluoric acid burns in contact with the skin, the mucosa, or the eyes. These burns are extremely painful and unless treated promptly may result in permanent damage, including loss of sight.

Chronic industrial fluorosis, called crippling fluorosis, has been reported in England, Scotland, the mainland of Europe, and Africa; crippling fluorosis, however, has never been seen in the United States.[1988] The disease is not rapidly reversible, and develops after exposures to relatively large amounts of fluoride over protracted periods. Exposures such that 20 to 80 mg or more of fluoride are ingested daily for periods of 10 to 20 years produce the full-blown disease. Crippling effects are limited to the skeleton,[1988] and include "poker back," painful and disabled joints, generalized osteoscleroses, calcification in the tendons and ligaments, and synostoses.[1492] Mottled teeth are a frequent sympton.[1492]

Threshold level value (TLV) for fluoride dusts is 2.5 milligrams per cubic meter as reported by the American Conference of Governmental Industrial Hygienists (ACGIH). The Federal Water Pollution Control Administration (FWPCA) Water Quality Criteria[0536] recommends permissible limit criteria for fluoride in drinking water ranging from 1.7 mg/liter to 0.8 mg/liter, for average daily maximum temperatures ranging from 50 to 90.5 F, and recommends that water for livestock use contain less than 2.4 mg/liter of fluoride ion. The same source[0536] indicates a quality requirement of a maximum of 1 mg/liter of fluoride ion in water intended for use by the canned, dried, and frozen fruits and vegetable industry.

Animal Toxicity

Because of the well-documented history and economic effects of fluorosis of farm animals, ingestion of fluoride has been investigated extensively in many species of animals. In general, symptoms of acute and lethal fluorine poisoning in animals follow those exhibited in man. Sub-acute dosages produce the symptoms of loss of appetite and starvation. Chronic effects, listed in order of appearance on exposed animals are:[1668]

1. Dental lesions (primarily damage to incisor teeth).
2. Hyperostosis.
3. Lameness.
4. Loss of appetite.
5. Decreased milk production.
6. Diminution in reproduction.

Herbivorous animals will exhibit the symptoms of acute fluorine poisoning on eating vegetation containing in excess of 5000 parts per million (ppm) of fluoride. Sub-acute effects were observed in cattle experimentally fed with vegetation containing 500 to 1200 ppm of fluoride, for time periods ranging from four months to six months.[1668]

Chronic effects, leading to economic losses occur on the continuous ingestion of food by dairy cattle containing 40 to 50 ppm of fluoride.[1665] Exposure terms of 5 years or more may be required for the maximum economic loss to occur. Susceptibility varies amongst animal species, ranging from maximum in dairy cattle, to the lower range in turkeys. The farm animals affected include dairy cattle, beef cattle, sheep, chickens, and turkeys.

Plant Toxicity

There are, in general, four types of fluoride effects on vegetation: Visible effects such as necrosis (injured portions of leaves die and become discolored); diminution in the growth or in the yield of fruit or seeds; changes in physiological activities, metabolic activities, and cellular structure with or without visible injury; and deposit or accumulation of fluoride in the plant with increasingly higher fluoride concentrations in its tissues.[1668] Plant species vary very widely in sensitivity to soluble fluorides. Sorghum, citrus, fruit trees, conifers and corn are relatively sensitive crops. Alfalfa is quite insensitive.

Comparatively little information is available for relating particulate fluoride levels to vegetation damage in contrast to the large collection of data on the effects of gaseous fluorides. Generally, the fluoride dusts are less toxic than the gaseous fluorides. Dissolved fluorides (NaF) have produced injury resembling that caused by HF in air. Fluoride damage to vegetation through fluoride contamination of the soil, while possible, has not been observed in the field, possibly because of the presence of sufficient calcium and aluminum in the soils to inactivate the fluoride[1668].

3. OTHER HAZARDS

The alkali and ammonium bifluorides, when moist or in solution, are extremely corrosive to glass, porcelain, and most common metals of construction. The bifluorides are non-flammable, but are easily decomposed on heating, yielding highly toxic HF fumes.

The alkali and ammonium fluorides and bifluorides are toxic to all life--yeast, other microorganisms, plant life, both harmful and beneficial--insects, fish and all higher vertebrates. Their use as economic poisons is based on this toxicity.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Care must be exercised in handling the alkali and ammonium fluorides to prevent contact of the materials with the skin or eyes, and to avoid ingestion by inhalation of dust or other means. Food should not be handled in proximity to the soluble fluorides. In case of contact with the bifluorides, the skin and eyes should be flushed with cold water for at least 15 minutes, and prompt medical attention should be secured. In the case of contact with the normal fluorides, the skin should be washed thoroughly; contact with the eyes requires medical attention in addition to thorough flushing with cold water. Contaminated clothing should be removed and washed before re-use.

The alkali and ammonium fluorides are shipped in screw cap bottles, for quantities up to 5 lb; for quantities from 5 lb to 400 lb, polyethylene bag-lined drums or fiber drums are used. In accordance with current manufacturers liability laws, the containers carry a "Poison" warning label, and information on treatment and antidotes for accidental contact and poisoning. The containers should be stored in a cool, dry area, and should be kept tightly closed.[2093, 2094, 2095, 2096]

Sodium fluoride shipped in interstate commerce must, as noted earlier, be colored blue, and must carry a Manufacturing Chemists Association (MCA) warning label. There are no current Department of Transportation or Coast Guard regulations which cover shipment or labeling of the other fluorides.

Recommended criteria for acceptable disposal of the alkali and ammonium fluorides are as follows:

Effluent and Environment	Maximum Concentration at Point Source	Basis for Recommendation
Particulate/other fluorides released to the air inside the plant boundaries.	2.5 mg/cubic meter (as F)	TLV, ACGIH[0025]
Particulate/other fluorides released to the air outside the plant boundaries.	0.25 mg	0.1 TLV
Alkali/ammonium fluorides released in water to natural watercourses or sewers.	Less than the concentration which will raise the receiving watercourse or sewer to 1.2 mg/liter of F.	FWPCA criteria[0536]

The stringency of the recommended criteria are due to both the acute and chronic toxicity of the soluble fluorides. Any excess of soluble fluorides released to a watercourse will not be decreased by natural action to acceptable levels for potable water supply, or for farm animal use unless the stream percolates through or runs over a limestone bed.

Particulate fluorides, released as aerosol fume, can cause both acute and chronic fluorosis in plant employees, and can cause economic damage to crops and farm animals in surrounding areas.

5. EVALUATION OF CURRENT AND NEAR FUTURE ALKALI AND AMMONIUM FLUORIDE DISPOSAL PROCESSES

Current Practices

The keystone of any economically feasible process for the minimum environmental impact disposal of any of the alkali or ammonium fluorides must involve either recovery of the fluoride portion of the compound or re-use, or precipitation of the fluoride as calcium fluoride, followed by separation and impact-free disposal of the calcium fluoride via use as a fluorspar substitute, or land burial. With the exception noted under Option Number 1, below, current practice in disposal of the alkali and ammonium fluorides is to vent the material without capture from high temperature operations such as glass manufacture, vitreous enamel processes, and brick manufacture,[1688] or to flush the fluoride wastes down the sewer after recovery of the economically valuable metal present.[0653] These practices are unacceptable. Two current disposal practices, and some possible future options are discussed in the following paragraphs.

Option Number 1--Tin and Fluoride Pollution Control Process. A patented process exists for the removal of both the tin and fluoride contents of plating, wash and tin recovery wastes from halogen tin lines used in tin plating.[0653] Basis for the process is the two-stage addition of lime slurry to the wastes in two sequential, compartmented reaction and settling tanks. The underflow from each tank is in part recycled to the feed, or reaction, compartment of the first tank. Most of the tin is precipitated in the first tank, and the part of the underflow from the first tank which is not recycled is sent to tin recovery operations. The majority of the fluoride is precipitated as calcium fluoride in the second tank. That portion of the underflow from the second tank which is not recycled is diverted to disposal operations. The overflow from the second tank is discharged to sewer.

The disposal system employed for the calcium fluoride waste product is not stated. To allow economic recovery, the discharged, alkaline CaF_2 slurry should be lagooned, and the clarified, fluoride-stripped overflow discharged to sewer. The separated CaF_2 should then be dried, and re-used as metallurgical grade CaF_2 in steel mill operations. Where economic recovery is not feasible, the sludge should be added to a landfill.

Option Number 2--Reaction with Slaked Lime. The disposal procedure given[0095] for package lots of the soluble inorganic fluorides in the laboratory is to add the fluorides slowly to a large container of water. Stir in a slight excess of soda ash and slaked lime. Allow the slurry to stand, settling, for 24-hrs. The supernatant liquor is then dicanted or siphoned into another container, and neutralized with dilute hydrochloric acid before being washed down into the sewer, with large quantities of water. The sludge is added to landfill.

Option Number 3--Discharge to the Environment. The majority of the sodium fluoride emitted by the glass industry[1668] is vented to the atmosphere. In those few cases where wet cyclones are employed, the sludge is frequently discharged to sewer. Both of these practices are undesirable.

In the enamel frit industry, about 80 percent of the plants discharge their NaF fume directly to the atmosphere.[1668] The remaining plants frequently discharge material recovered from stack gas to the sewer, without treatment. These practices are undesirable, and are not recommended.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The alkali and ammonium fluorides are not candidates for National Disposal Sites. Their treatment by either of the techniques listed below as recommended procedures is not hazardous, does not require costly or sophisticated apparatus, and is economically feasible and technologically practical for waste generation site use.

The procedure recommended for treatment of large quantity, continuous discharges of the alkali and ammonium fluorides is that of Option Number 1--i.e., continuous reaction with an excess of lime, followed by lagooning, and either recovery or landfill disposal of the separated CaF_2. The procedure recommended for the treatment of package lots and spills of the alkali and ammonium fluorides is that of Option Number 2--i.e., reaction in solution with an excess of alkalid lime, followed by separation of CaF_2, and landfill disposal of the separated CaF_2.

7. References

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2093 Product Information Data Sheet. Ammonium Fluoride, crystal, technical. NH_4F DA-32672 New York, General Chemical Division, Allied Chemical. 2 p.

2094 Product Information Data Sheet. Potassium Fluoride, anhydrous purified. KF DA-40913 Morristown, New Jersey, Industrial Chemicals Division, Allied Chemical, 1967. 2 p.

2095 Product Information Data Sheet, Potassium Fluoride, crystal, purified. $KF\ 2H_2O$. DA-41042 New York, General Chemical Division, Allied Chemical. 2 p.

2096 Product Information Data Sheet. Potassium Bifluoride, crystal, technical. KF. HF DA-41462 New York, General Chemical Division, Allied Chemical, 1961. 2 p.

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Ammonium Fluoride

IUC Name Ammonium Fluoride

Common Names Neutral Ammonium Fluoride

Structural Formula

NH_4F

Molecular Wt. 37.04 Melting Pt. Sublimes(1) Boiling Pt. Sublimes (1)

Density (Condensed) 1.315 @ 25 °C(2) Density (gas) - @ - ° -

Vapor Pressure (recommended 55 C and 20 C)

- @ - ° - @ - ° - @ - °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water 41.8 g/100g soln@0 C Hot Water 54.1g/100g soln@0 Ethanol Slightly Sol.

Others:

Acid, Base Properties Aqueous solution acid

Highly Reactive with Quinine salts; soluble calcium salts

Compatible with iron (dry)

Shipped in Plastic (polyethylene) bag lined drum; fiber drum (3)

ICC Classification None Coast Guard Classification None

Comments Salt is deliquescent. Commercial salt is granular powder. Used in etching and frosting glass; as antiseptic in brewing beer; preserving wood; moth proofing agent.(2)

References (1) 0766
(2) 1433
(3) 2093

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Ammonium Bifluoride

IUC Name Ammonium Hydrogen Fluoride

Common Names Ammonium Acid Fluoride

Structural Formula

NH_4HF_2

Molecular Wt. 57.05 Melting Pt. 126.1 C Boiling Pt. Subl.

Density (Condensed) 1.503(2) @ - ° - Density (gas) - @ - ° -

Vapor Pressure (recommended 55 C and 20 C)

- @ - ° - @ - ° - @ - °

Flash Point - ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water 28.45g/100gsoln@0 C Hot Water 85.55g/100gsoln@100 C Ethanol Slightly sol.

Others: -

Acid, Base Properties Strongly acid in solution

Highly Reactive with glass; silica

Compatible with polyethylene; plastics; rubber; wood; parafinned paper and fiberboard

Shipped in polyethylene lined drums

ICC Classification None Coast Guard Classification None

Comments Used to etch/frost glass; as antiseptic in brewing beer; moth proofing(1); removal of silica scale (boilers, etc.); oil well treatment; fungicide; laundry soap; in the manufacture of Mg and Mg alloys.

References (1) 1433
(2) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium Fluoride

IUC Name Potassium Fluoride

Common Names Potassium Fluoride

Structural Formula

KF

Molecular Wt. 58.10   Melting Pt. 860 C(1)   Boiling Pt. 1505 C(1)

Density (Condensed) 2.481(1) @ - ° -   Density (gas) - @ - ° -

Vapor Pressure (recommended 55 C and 20 C)

- @ - °   - @ - °   - @ - °

Flash Point - °   Autoignition Temp. - °

Flammability Limits in Air (wt %)   Lower -   Upper -

Explosive Limits in Air (wt. %)   Lower -   Upper -

Solubility

Cold Water 92.3 g/100 ml@18 C   Hot Water Very sol.   Ethanol Insol.

Others: Sol liquid NH_3

Acid, Base Properties

Highly Reactive with glass, porcelain (corrodes)

Compatible with Aluminum (anhydrous)

Shipped in Polyethylene bag lined drums; screw cap bottles(3)

ICC Classification None   Coast Guard Classification None

Comments Used as silver soldering flux, preparation of barium titanate crystals(2).
Hydrates very readily to $KF.2H_2O$

References (1) 1492
(2) 1433
(3) 2094

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium Bifluoride

IUC Name Potassium Hydrogen Fluoride

Common Names Potassium Acid Fluoride
Fremy's salt

Structural Formula KHF_2

Molecular Wt. 78.10 Melting Pt. 239 C (B)(1) Boiling Pt. Decomposes

Density (Condensed) 2.37 (2) @ - ° - Density (gas) - @ - ° -

Vapor Pressure (recommended 55 C and 20 C)

- @ - ° - @ - ° - @ - °

Flash Point - ° Autoignition Temp. - °

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water 24.5g/100m/@0 C Hot Water 114g/100m/@80 C Ethanol Insol

Others: -

Acid, Base Properties Strongly acid

Highly Reactive with Glass; silica

Compatible with Plastics; rubber

Shipped in Polyethylene-lined drums; screw cap bottles(3)

ICC Classification Coast Guard Classification

Comments Used in silver soldering fluxes; frosting glass; anti-fungal agent for wood; electrolyte for fluorine manufacture. Decomposes on heating, into KF and HF.(2)

References (1) 1433
(2) 1492
(3) 2096
-

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Sodium Fluoride

IUC Name Sodium Fluoride

Common Names Villiaumite

Structural Formula

NaF

Molecular Wt. 42.00 Melting Pt. 993 C(1) Boiling Pt. 1704 C(1)

Density (Condensed) 2.78 @ - ° - Density (gas) - @ - ° -

Vapor Pressure (recommended 55 C and 20 C)

- @ - ° - @ - ° - @ - °

Flash Point ° Autoignition Temp. - °

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water 4g/100ml @ 0 C Hot Water 5g/100ml @ 100 C Ethanol V. slight. sol.

Others:

Acid, Base Properties Solution in water is basic

Highly Reactive with -

Compatible with plastics; rubber; paper

Shipped in 100 lb multiwall bags and 125 and 400 lb fiber drums

ICC Classification MCA warning label Coast Guard Classification None

Comments Used as insecticide; pesticide; in vitreous enamel and glass mixes; as steel degassing agent; in flux in fluoridating water; in electroplating. Sodium fluoride sold for insecticide uses must be colored blue. Poison label required by some states.(2)

References (1) 1492
(2) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium Bifluoride

IUC Name Sodium Hydrogen Fluoride

Common Names Sodium Acid Fluoride

Structural Formula

$NaHF_2$

Molecular Wt. 62.01 Melting Pt. Decomposes Boiling Pt. Decomposes

Density (Condensed) @ Density (gas) - @ - -

Vapor Pressure (recommended 55 C and 20 C)

- @ - - @ - - @ -

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water 3.25g/100ml@20 C(1) Hot Water 7.5g/100ml@90 C(1) Ethanol -

Others:

Acid, Base Properties Solution is acid

Highly Reactive with glass; steel

Compatible with

Shipped in 100 lb multiwall bags; 125,375 and 400 lb fiber drums

ICC Classification Coast Guard Classification

Comments Used as laundry "sour", in bleaching leather; disinfecting hides; plating tin; etching/frosting glass; cleaning stone and brick(1) Decomposes on heating, to NaF and HF.

References (1) 1433

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PROFILE REPORTS ON THE ANTIMONY FLUORIDES

Antimony Pentafluoride (36), Antimony Trifluoride (43)

1. GENERAL

Introduction

Antimony pentafluoride and antimony trifluoride are included in a combined profile report because of similarities in chemistry, toxicology, other hazards and industrial uses.

Antimony Pentafluoride

Antimony pentafluoride is a colorless, hygroscopic, corrosive moderately viscous, oily liquid. The compound has an appreciable vapor pressure at room temperature, and fumes in air, with hydrolysis to HF. The physical and chemical properties of SbF_5 are summarized in the attached worksheet.

The large scale production of SbF_5 is accomplished by the addition of an excess of anhydrous hydrogen fluoride to antimony pentachloride in an all-aluminum apparatus.[1988] The mixture is agitated during the addition of the HF, except for the mid-stage of the reaction, during which intermediate solid chlorofluorides are formed. The anhydrous HF is refluxed over the mixture until all of the chlorine has been displaced as HCl, in accordance with the reaction:

$$SbCl_5 + 5HF \rightarrow 5HCl + SbF_5$$

The HCl is driven off by distillation, followed by the excess HF.

The major uses of antimony pentafluoride are:

1. The preparation of organic fluorine compounds, either alone or in combination with hydrogen fluoride, iodine pentafluoride, or antimony pentachloride.
2. The substitution of fluorine for chlorine in chlorinated hydrocarbons.

3. The formation of complex compounds with other metal salts and halogens.

4. The preparation of inorganic fluorides by reaction with P_4O_{10}, $MoCl_5$, CrO_2Cl_2, PCl_3, and other similar compounds.

The most important fluorinating agent for industrial fluorinations is hydrogen fluoride in the presence of antimony (V) compounds. Sb (V) is the most useful and most effective catalyst, and SbF_5 is the most effective fluorinating agent.

Antimony Trifluoride

Antimony Trifluoride is a white deliquescent crystalline solid. The commercial salt frequently contains antimony oxide or a basic salt. The crystal lattice is molecular in character, although the chemical reactions of the compound are most frequently ionic.[1988] SbF_3 is extremely soluble in water, in which it undergoes a limited hydrolysis. The physical and chemical properties of SbF_3 are summarized in the attached worksheet.

Antimony trifluoride may be prepared by crystallization from a solution of Sb_2O_3 in excess hydrofluoric acid. The more common method of manufacture is by reacting $SbCl_3$ and excess anhydrous HF. Hydrogen chloride is evolved at 0-15 C; excess hydrogen fluoride is distilled off at 40-50 C; unreacted $SbCl_3$ is removed by extraction with carbon tetrachloride.

The major uses of antimony trifluoride are:

1. To catalyze fluorination of organic compounds by anhydrous HF.

2. To manufacture organic chlorofluorides by metathesis.

3. In the form of the sodium fluoride and ammonium sulfate double salts, in dyeing.

4. In the manufacture of pottery and porcelains.

The fluorinating power of the antimony fluorides varies from relatively mild antimony (III) fluoride through mixtures of antimony (III) fluoride and antimony (V) chloride to very powerful antimony (V) fluoride. A moderately high degree of selectivity is achieved in the substitution of fluorine for the other halogens by proper choice of antimony fluoride.[2027]

Antimony (III) fluoride is only slightly more active than hydrogen fluoride and behaves similarly when mixed with HF. It will, however, give substitution in a dialkyldichloromethane, in contrast to HF. The order of strengths cited above has been summarized as follows:[2027]

$$SbF_3 < (SbF_3 + SbCl_3) < (SbF_3 + SbCl_5) < SbF_3Cl_2 < SbF_5$$

2. TOXICOLOGY

Human Toxicity

The antimony florides produce physiological responses exhibiting the combined effects of soluble antimony compounds and soluble fluorides. For antimony (V) fluoride (SbF_5),caustic effects similar to those of hydrofluoric acid are superimposed upon the toxicity due to soluble antimony and soluble fluoride compounds.[1492]

Specifically, exposure to soluble antimony compounds causes dermatitis, keratitis, ulceration of the nasal septum,[1492] complaints referable to the nervous system (irritability, sleeplessness, fatigue and dizziness), pneumonitis, fatty degeneration of the liver, a decreased leucocyte count, and damage to the heart muscle.[0766] Symptoms in most cases include intense gastric and intestinal irritation, with epigastric pains, dysphagia, a metallic-like taste, vomiting of blood-stained material, tenesmus, watery diarrhea, rapid pulse, profuse sweating, and spasms of the muscles of the extremities. In fatal cases, cyanosis, subnormal temperature, delirium and collapse may also occur. A lethal dosage as low as 3 grains, taken in 1 1/2 grain encrements over a 24-hr interval has been reported,[2028] but larger doses have been non-lethal.

Chronic poisoning due to ingestion/inhalation of soluble antimony compounds may occur, with symptoms of anorexia, nausea, vomiting, thirst, diarrhea, muscular cramps and cold sweats.[2028]

The TLV for antimony compounds is 0.5 mg/cubic meter;[0766] the recommended exposure level for SbF_5 is 0.0005 mg/cubic meter/24 hrs.

The effects of soluble fluorides include nausea and vomiting, salivation, burning, cramp-like abdominal pains, diarrhea, dehydration and thirst; muscle weakness, central nervous depression, cyanosis, shock, weak and thready pulse, shallow unlabored respiration, weak heart tones, paralysis of the muscles of deglutation, carpopedal spasm, spasm of the extremities, and, in extreme cases, death. Anhydrous SbF_5, or highly concentrated solutions, produces burns similar to those of HF; these burns are usually more severe than those from the other mineral acids.[1988] External contact causes severe irritation of the eyes and eyelids,[2023] resulting in prolonged or permanent visual defects or total destruction of the eyes. Inhalation may cause extreme irritation of the respiratory tract, pulmonary inflammation, and congestion. Ingestion causes necrosis of the esophagus and stomach, with the additional symptoms noted above. The skin is burned by SbF_5,[2023] and severely irritated by SbF_3.[1492]

Lethal dosages of 1 1/2 to 2 grams (25 to 30 grains), expressed as F, of soluble fluoride have been reported[1988]; prompt treatment has averted death with much larger quantities.[1988] Chronic fluoride poisoning, reported for other soluble fluorides from exposures to relatively large (but sub-acute) dosages of fluoride over protracted periods, is improbable with the antimony fluorides, since the acute toxic effects due to antimony would supervene at the dosages indicated (ranging from 20 to 80 mg or more of fluoride per day[1988]).

The Federal Water Pollution Control Administration (FWPCA) report on "Water Quality Criteria"[0536] did not establish concentration limits for antimony in public water supplies, although mention was made of potential toxicity.

Aquatic Toxicity

Antimony fluoride has been reported as lethal to fish in concentrations which range from 100 to 200 parts per million.[1988] A dose of 5 mg (injection) was lethal to frogs.[1988]

3. OTHER HAZARDS

Antimony trifluoride and antimony pentafluoride solutions are highly corrosive to most metals, due to the highly acid properties of the salt-water systems. Antimony pentafluoride, anhydrous, corrodes glass, copper and lead,[1492] and attacks paper, wood, rubber, and many plastics.[1988] Neither salt is flammable, but both are easily volatilized, to give toxic fumes.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Great care must be exercised in handling antimony pentafluoride, because of its volatility and hazardous, highly reactive character. A face shield, neoprene gloves, and protective clothing are recommended in the handling of SbF_5.[2023] Material spilled on the skin should be immediately flushed away with large quantities of cold water until all of the compound is removed (up to 4 hours, or until medical attention is obtained), paying particular attention to the skin under the nails. Prompt medical attention is required. Where medical attention is delayed, a mixture of glycerin and magnesium oxide should be applied.[2023] Clothing which has been contaminated should be removed and washed before re-use. If any SbF_5 gets into the eyes, prompt medical attention is absolutely necessary. The eyes should be flushed immediately with cool water for 15 to 30 minutes.[2023] Personnel handling SbF_5 should avoid breathing the vapor.

Antimony pentafluoride is shipped in steel cylinders (1,5,25, and 200 lb SbF_5 content) and, in accordance with DOT regulations, must carry a "Corrosive liquid" white label when shipped in interstate commerce or by boat. The cylinders should be stored outdoors, protected from the weather, or in a well-ventilated room. Exposure to fire or direct heat should be avoided.[2023]

Since antimony trifluoride is a solid, handling hazards are less than those involved with antimony pentafluoride. The same general precautions should, however, be taken in handling SbF_3 as are listed above for SbF_5.

There are no current Department of Transportation or Coast Guard regulations which cover shipment or labeling of antimony trifluoride. Polyethylene containers are used for shipping the material.

Criteria for acceptable disposal of the antimony fluorides do not currently exist. It is recommended, in view of the potential chronic toxicity of antimony ingested over a protracted period, that tentative limits for antimony fluorides in receiving streams be set at the same level as those set for arsenic in potable water,[0536] where a concentration of 0.05 mg per liter is cause for rejection.

5. EVALUATION OF PRESENT WASTE MANAGEMENT PRACTICES

The major use of the antimony fluorides is as catalysts and fluorine carrier in the manufacture of fluorocarbons. The amounts of all fluorides emitted to the environment from the fluorocarbon manufacturing processes are extremely small. Because of the highly toxic and corrosive nature of the feed and catalyst materials, extreme care is taken to control spills and leakage. All product streams are scrubbed to meet purity specifications; the unreacted HF is removed as solid CaF_2 and disposed of in that form.[1688] There are no gaseous effluent streams. For these reasons, current practices for prevention of antimony fluoride waste discharge from the fluorocarbon manufacturing processes are deemed completely satisfactory.

There are no procedures reported for the disposal of small quantities of the antimony fluorides, with the exception of advice not to use water on fires involving antimony pentafluoride.[0094]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Manufacturing process effluent streams containing the antimony fluorides can be best handled at the sites where they originate by the continuation of current, acceptable disposal processes. Small contaminated or surplus quantities of antimony trifluoride and antimony pentafluoride should either be returned to the manufacturers for reprocessing, or disposed of at National Disposal Sites. The disposal method to be employed at the National Disposal Sites will require development. A proposed disposal process is to combine Methods 27d and 11 of the Manufacturing Chemists Association "Laboratory Waste Disposal Manual."[0095] Briefly stated, the disposal concept is as follows:

> Dissolve the antimony fluoride in the minimum quantity of dilute hydrochloric acid. Saturate with hydrogen sulfide. Filter wash and dry the antimony sulfide precipitate; sell the precipitate to a primary antimony metal producer. Air strip the filtrate of dissolved H_2S, passing the effluent air into a controlled incineration device, equipped with a lime scrubber. React the stripped filtrate with an excess of lime; evaporate to dryness, and dispose of the lime-CaF_2-$CaCl_2$ mixture by land burial.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Antimony Trifluoride

IUC Name Antimony (III) Fluoride

Common Names Antimonous Fluoride

Structural Formula

SbF_3

Molecular Wt. 178.75 Melting Pt. 292 C (2) Boiling Pt. 376 C (3)*

Density (Condensed) 4.379(s) @ 20.9 C Density (gas) ------- @ ---- ° -------

Vapor Pressure (recommended 55 C and 20 C)

3mm @ 17 C (1) 107mm @ 62 C (1) ----- @ -------- °

Flash Point -------- ° Autoignition Temp. --- °

Flammability Limits in Air (wt %) Lower -------- Upper -------

Explosive Limits in Air (wt. %) Lower -------- Upper -------

Solubility

Cold Water 384.7g/100g @ 0 C (1) Hot Water ------------ Ethanol -----------

Others: --------

Acid, Base Properties Undergoes limited hydrolysis with water to form HF.

Highly Reactive with

Compatible with Glass and steel, if dry.

Shipped in Glass containers or steel drums

ICC Classification None Coast Guard Classification None

Comments SbF_3 is used as a fluorinating agent in the Swarts Reaction. Forms salts of the type K_2SbF_5, Na_3SbF_6 with metal fluorides. Double salts are used in dyeing. Also used in the manufacture of pottery and porcelains.

References (1) 1988
(2) 1433
(3) 1492

* Sublimes @ 319 C

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Antimony Pentafluoride

IUC Name Antimony (V) Fluoride

Common Names Antimony Pentafluoride

Structural Formula

SbF_5

Molecular Wt. 216.74 Melting Pt. 8.3 C (1) Boiling Pt. 142.7 C (1)

Density (Condensed) 3.145 (liq.) @ 15.5 C(1) Density (gas) ---- @ --- ° ------

Vapor Pressure (recommended 55 C and 20 C)

4.3mm @ 25 C(4) 18mm @ 50 C(1) 170mm @ 100 C(1)

Flash Point --------- ° Autoignition Temp. --- °

Flammability Limits in Air (wt %) Lower -------- Upper -------

Explosive Limits in Air (wt. %) Lower -------- Upper -------

Solubility

Cold Water Sol., with reaction. Hot Water ---------- Ethanol Reacts

Others: -----------

Acid, Base Properties Solution in water strongly acid.

Highly Reactive with water, to form $SbF_5.2H_2O(s)$. Corrodes glass, copper and lead.(3) Attacks skin, paper, wood, rubber.(1)

Compatible with steel when dry. May be stored in aluminum when dry.

Shipped in 1, 5, 25, 200 lb. steel cylinders.(2)

ICC Classification Corrosive liquid; white label Coast Guard Classification Corrosive liquid; white label.

Comments Fumes in air, with hydrolysis to HF(2). Forms $HSbF_6$ with HF; many metallic Fluoroantimonate salts are known. Used as fluorinating agent. Reacts with P_4O_{10}, $MOCl_5$, CrO_2Cl_2 and organochlorine compounds to yield hydro-compounds. Hygroscopic, corrosive, moderately viscous liquid. Forms addition compounds with halogens and many organics.

References (1) 1988 (4) 2023
(2) 1996
(3) 1492

PROFILE REPORTS ON

Barium Compounds

Barium Carbonate (52), Barium Chloride (53), Barium Cyanide (469) Barium Nitrate (471), Barium Sulfide (472)

1. GENERAL

Introduction

Barium compounds exhibit a close relationship to the compounds of the other alkaline earth metals, calcium and strontium. Barium behaves generally as a bivalent element, as do the other alkaline earth metals. The solubilities of barium salts are typical of the alkaline earth group. The halides and nitrate are quite soluble, whereas the carbonate and sulfate are insoluble. With the exception of barium sulfate, the salts dissolve partially in carbonic acid and completely in hydrochloric or nitric acid. The sulfate is extremely insoluble and is useful for the determination of the barium ion.[0646]

Precipitated barium carbonate is the most important of the manufactured pure barium chemicals. In production tonnage it is second to the principal mineral, barite. The production of barium carbonate has decreased considerably in the last few years. In 1969, there were 114,000 tons of barium carbonate produced in the United States.[1506] In 1970 the production of barium carbonate declined to 61,083 tons. In that same year the production of all other barium compounds totaled 57,000 tons. Of that total it is estimated that there were less than 10,000 lbs of barium cyanide produced.[1814] Individual production figures for the other barium compounds discussed in this profile report are not available.

Manufacture

All major barium salts in the U.S. are produced from the chemical grade of barite ($BaSO_4$). Since barite is highly insoluble, the starting point of the barium-plant process is the reduction of barite to soluble barium sulfide or black ash. This is then converted to the various barium compounds.

Barium Carbonate. Black ash is dissolved in water and its clear solution is the usual raw material for barium carbonate manufacture. There are two basic methods of manufacture which differ mainly in the way the carbonate ion is introduced.

$$BaS + Na_2CO_3 \longrightarrow BaCO_3 + Na_2S \qquad (1)$$

$$BaS + CO_2 + H_2O \longrightarrow BaCO_3 + H_2S \qquad (2)$$

The product from the straight-gassing process (equation 2) is more impure than the soda ash product (equation 1). Large scale commercial facilities for the manufacture of barium carbonate include the following[1506]:

Barium and Chemicals Incorporated, Painesville, Ohio
Chemical Products Corporation, Cartersville, Georgia
FMC Corporation, Modesto, California
Sherwin-Williams Company, Coffeyville, Kansas.

Barium Chloride. Barium chloride is produced by treating a barium sulfide solution with hydrochloric acid:

$$BaS + 2HCl \longrightarrow BaCl_2 + H_2S$$

Barium Cyanide. Barium cyanide ($Ba(CN)_2$) is prepared by reaction of hydrogen cyanide on barium hydroxide suspended in pretroleum ether. The dihydrate is formed and then dried carefully under vacuum to yield a product of 95 percent purity. Barium cyanide is produced by Phillips Brothers Chemicals, Incorporated, New York.

Barium Nitrate. Barium nitrate is made by the interaction of a suspension of barium carbonate in a mother liquor with nitric acid, followed by crystallization after filtration. Another method is to dissolve sodium nitrate in a saturated solution of barium chloride, with subsequent precipitation of barium nitrate. The precipitate is centrifuged, washed and dried. Barium nitrate is produced by Barium and Chemicals Incorporated, Painsville, Ohio.

Barium Sulfide. Black ash is produced by reducing ground barite with coal at high temperatures. The reaction is:

$$BaSO_4 + 2C \longrightarrow BaS + 2CO_2$$

Barium sulfide is also produced by Barium and Chemicals, Incorporated, Painsville, Ohio.

Uses

The principal application areas of the five barium compounds have been summarized by Miner (Table 1).[646]

Sources and Types of Barium Wastes

The sources of barium wastes may include the following: (1) barium compound manufacturers; (2) barium compound wholesalers; (3) commercial and industrial processes including those from paper manufacturing plants, ceramic and enamel manufacturing plants, etc.

In general, barium wastes can be classified as either diluted or concentrated wastes. Diluted barium wastes include those generated in the waste waters of manufacturers and possibly spent solutions used to clean empty barium compound containers. Concentrated barium wastes include any unused or contaminated barium compounds and barium compounds left in containers after emptying.

Physical and Chemical Properties

The physical and chemical properties of the five barium compounds are included in the attached worksheets.

2. TOXICOLOGY

Soluble barium compounds are highly toxic when ingested, while insoluble compounds, such as barium sulfate, are generally nontoxic. Inhaled barium compounds cause a benign pneumoconiosis, called baritosis. Ingestion of soluble barium compounds results in strong stimulation of the muscles, including the heart; irritation of the intestinal tract; and irritation of the central nervous system.[0646]

The symptoms of barium poisoning are severe abdominal pain with vomiting, dyspnoea, rapid pulse, paralysis of the right arm and leg, and eventually cyanosis and death. The usual result of exposure to the sulfide and carbonate is irritation of the eyes, nose and throat, and of the skin, producing dermatitis.[0766]

The five barium compounds included in this profile report are all highly toxic and exhibit similar toxicity symptoms. With barium cyanide, however, the toxic effects of both elements of the compound must be considered (refer to Profile Report on Cyanides).

The relative oral LD_{50} values to the rat are 50-200 mg/kg for barium carbonate and 355-533 mg/kg for barium chloride.[0646] The estimated oral LD_{50} values for man are 55 mg/kg for barium carbonate and 80 mg/kg for barium chloride. The American Conference of Governmental Industrial Hygienists (1971) recommended a Threshold Limit Value (TLV) in air of 0.5 mg/M^3 for all soluble barium compounds. For cyanides ($Ba(CN)_2$) the TLV in air is 5.0 mg/M^3.[0225] The U.S. Public Health Service established the permissible criteria for barium in public water supplies as 1.0 ppm. This agency also recommends that the concentration of cyanides be kept below .01 ppm for both fish and people.[1752]

3. OTHER HAZARDS

Barium nitrate is an oxidizing material. In contact with easily oxidizable substances it may react rapidly enough to cause ignition, violent combustion, or explosion. It increases the flammability of any combustible substance.[0096]

The fire hazard of barium sulfide by spontaneous chemical reaction is moderate; air, moisture or acid fumes may cause it to ignite. Barium sulfide may react violently and explosively on contact with powerful oxidizers.[0766]

Other than the toxic effects, barium carbonate, barium chloride and barium cyanide present no further hazardous problems.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Care should be exercised in handling barium compounds because of their high toxicity. The use of rubber gloves is advisable. Any material which comes in contact with the skin should be immediately removed with plenty of soap and water.

Barium nitrate should be stored in an area where it will be separated from combustible, organic or other readily oxidizable materials. Avoid storage on wood floors. Any spilled nitrate should be immediately removed and disposed of.[0096] All of the barium compounds discussed in this report should be stored away from foodstuffs, feeds, or any other material intended for consumption by humans or animals.

Adequate procedures for the transportation of barium cyanide and barium nitrate have been established by the Department of Transportation.[0278] Label requirements, as well as the maximum quantities permitted to be shipped in one outside container, are also specified.

Disposal/Reuse

Disposal or reuse of waste barium compound streams must take into account the toxic nature of these materials. The discharged barium compounds must be treated by the methods described in Section 5 or diluted to a concentration of 1 ppm (.01 ppm for $Ba(CN)_2$).

The safe disposal of barium compounds is defined in terms of the recommended maximum concentrations released to the atmosphere and a potable water source. These recommended maximum concentrations are as follows:

Contaminant in Air	Maximum Concentration & Point Source Release Rate	Basis for Recommendation
Barium Carbonate	.005 mg/M^3/24 hours	.01 TLV
Barium Chloride	.005 mg/M^3/24 hours	.01 TLV
Barium Cyanide	.005 mg/M^3/24 hours	.01 TLV
Barium Nitrate	.005 mg/M^3/24 hours	.01 TLV
Barium Sulfide	.005 mg/M^3/24 hours	.01 TLV

Contaminant in Water	Maximum Allowable Concentration	Basis for Recommendation
Barium Carbonate	1 mg/l	U.S.Public Health Service recommendation for public drinking water.
Barium Chloride	1 mg/l	"
Barium Nitrate	1 mg/l	"
Barium Sulfide	1 mg/l	"
Barium Cyanide	.01 mg/l	"

It should be noted that the recommended maximum allowable concentrations for the barium compounds (except barium cyanide) in water are less than that of .01 of the TL_m for fish.[1752] The maximum allowable concentration of barium cyanide in public drinking water (.01 mg/l) is also a safe level for fish. It was found that trout could survive a cyanide concentration of .02 mg/l for more than 27 days.[1752]

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Dilute Waste

Option No. 1 - Precipitation. By far the most widespread method used for removing barium from industrial waters is precipitation with sulfate ion (usually sulfuric acid) in settling ponds.[1794] The precipitate formed, $BaSO_4$, is quite insoluble and the resulting effluent from the pond contains about 2 ppm of barium. This effluent would then be diluted with an equal amount of water to meet the permissable criteria for barium in public water supplies (1.0 ppm). Precipitation and settling is normally a slow procedure and with high effluent flow it is normally necessary to have settling ponds or lagoons in which to allow the slow coagulation process to occur, the clear effluent removed and the precipitate dried. Since barium sulfate is important in the barium industry (see section on Manufacturing) it can be economically recycled. This method can be used for both concentrated and dilute barium wastes. In the case of barium cyanide wastes, the cyanide should be removed first before precipitating the barium with sulfuric acid. The primary method for removing cyanide is to oxidize it to CO_2 and N_2 with an alkaline chlorine solution. Other methods for removing cyanide include ion exchange, electro-oxidation, and reaction with aldehydes (refer to Profile Report on cyanides for additional information). Barium could also be precipitated by chromate ion to form barium chromate. This is a workable method but is not normally economically feasible unless a market as pigments for the preciptate is available.

Option No. 2 - Ion Exchange. Ion exchange can be used to remove barium from dilute aqueous waste streams. Barium will behave much like calcium and magnesium and can be removed from an aqueous waste stream by either a sulfonic acid type cation exchange resin or a carboxylic weak acid type resin, depending upon the pH of the stream.[1795] An ion exchange unit cannot usually handle an influent concentration load above 1500 ppm. An advantage of ion exchange is that due to the concentrative effects it is possible to apply this process in recycling barium materials or in concentrating wastes for transport to centralized disposal. The major difficulty in ion exchange operation is the critical dependence on flow rate. The ion exchange system is designed to operate with a particular efficiency at a certain set flow. Should this flow be exceeded for even short periods of time, the efficiency for adsorbing the barium ion decreases drastically causing the effluent to exceed the permissible limit.

Option No. 3 - Reverse Osmosis. The effectiveness of reverse osmosis to remove barium from water has been investigated by Sourirajan.[1812] Following passage of a barium waste stream through a porous cellulose acetate membrane, it was found that the barium concentration was reduced from 34.35 g/liter to 7.35 g/liter. It is conceivable that "R.O." is applicable to dilute barium salt solutions as well, but no data is available to support this assertion. With an effluent concentration of 7.35 g/liter, the "R.O." unit would have to be used in conjunction with some other process (ion exchange for example) to produce an effluent with a permissible concentration of barium.

Option No. 4 - Adsorption on Activated Carbon. Activated carbon has been shown to remove barium from acetate solutions by Kuzin et al.[1813] Although the laboratory investigation was principally directed towards the separation of uranium from other metallic compounds; it was found in the same study that activated carbon possessed a sorption capacity for soluble barium compounds of 0.7 mg/g carbon, thus demonstrating the feasibility of activated carbon adsorption as a near future process for removing soluble barium compounds from water.

The processes mentioned above deal exclusively with barium wastes in the conventional aqueous form. If, however, the barium wastes are present in the solid form, the usual methods for removal of solids, such as bag filters, electrostatic precipitation, and wet scrubbers should prevent their escape to the atmosphere.[0646]

The best method for disposing of both dilute and concentrated aqueous barium wastes is precipitation with sulfate ion. The technique is efficient and adequate for large scale removal of barium.

The other processes discussed (ion exchange, reverse osmosis, and adsorption on activated carbon) will result in reduced amounts of waste barium but are not applicable as primary treatment methods. These processes should function mainly as a secondary treatment of the effluent from a barium precipitative facility.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Considering the provisions for the recycle and recovery of waste barium by the producers, it is felt that barium compounds do not warrant National Disposal Site treatment. The precipitation method for the removal of barium from waste streams is inexpensive enough for even the small barium manufacturers and users to operate.

In summary, the recovery and/or disposal of barium wastes is currently handled adequately at the industrial site level and this mode should be continued.

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#52

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Barium Carbonate

IUC Name

Common Names

Structural Formula

$BaCO_3$

Molecular Wt.[1] 197.37 Melting Pt.[2] 1740 @ 90 atm Boiling Pt. Decomposes

Density (Condensed) 4.43 @ ° Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.0022g/100g @ 16 C Hot Water 0.0065 g/100g @ 100C Ethanol insoluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Bags, barrels and kegs

ICC Classification Coast Guard Classification

Comments White powder

References (1) 0766.
(2)
(3)

---

[1] Give a reference for each entry.

[2] Supply units where necessary

#53

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Barium Chloride

IUC Name

Common Names

Structural Formula

$BaCl_2$

Molecular Wt.[1] 208.27 Melting Pt.[2] 925 C Boiling Pt. 1560 C

Density (Condensed) 3.856 @ 24 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 37.5g/100g @ 26 C Hot Water 59 g/100g @ 100 C Ethanol insoluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Bags, barrels and kegs

ICC Classification Coast Guard Classification

Comments

References (1) 0766.
(2)
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

#469

H. M. Name Barium Cyanide

IUC Name

Common Names

Structural Formula

$Ba(CN)_2$

Molecular Wt.[1] 189.40 Melting Pt.[2] Slowly decomposes Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 1 gm/1.5ml Hot Water Ethanol 1 gm/20ml

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Bags, barrels and kegs

ICC Classification Coast Guard Classification

Comments

References (1)

(2)

(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

#471

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Barium Nitrate

IUC Name

Common Names

Structural Formula

$Ba(NO_3)_2$

Molecular Wt.[1] 261.38 Melting Pt.[2] 592 C Boiling Pt. Decomposes

Density (Condensed) 3.24 @ 23 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 8.7g/100cc Hot Water 34.2g/100cc Ethanol Insoluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Bags, barrels, kegs, casks, drums

ICC Classification Coast Guard Classification

Comments In contact with easily oxidizable substances it may react rapidly enough to cause ignition, violent combustion or explosion.

References (1) 0766.
(2) 0096.

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[1] Give a reference for each entry.

[2] Supply units where necessary

#472

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Barium Sulfide

IUC Name

Common Names

Structural Formula

BaS

Molecular Wt.[1] 169.43 Melting Pt.[2] 1200 C Boiling Pt.

Density (Condensed) 4.25 @ 15 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Soluble Hot Water Soluble Ethanol Insoluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Bags, barrels, kegs

ICC Classification Coast Guard Classification

Comments May react violently and explosively on contact with powerful oxidizers.

References (1)

(2)

---

[1] Give a reference for each entry.

[2] Supply units where necessary

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TABLE 1[0646]

APPLICATION AREAS OF BARIUM COMPOUNDS

Compound	Uses
Barium Carbonate, $BaCO_3$	As rat poison; in ceramics, enamels; in manufacture of paper, barium salts, optical glasses; in case-hardening steels.
Barium Chloride, $BaCl_2$	In manufacturing of blanc fixe (precipitated $BaSO_4$); as mordant for acid dyes; in weighting and dyeing textile fabrics; as boiler compounds for softening water; as purifying agent in brines; in manufacture of barium colors and of chlorine and sodium hydroxide; as flux for magnesium alloys, in case hardened steels.
Barium Cyanide, $Ba(CN)_2$	In electroplating processes.
Barium Nitrate, $Ba(NO_3)_2$	In manufacture of BaO_2; as pyrotechnic for green fire; as green signal lights; in the vacuum tube industry.
Barium Sulfide, BaS	As raw material for other barium compounds.

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PROFILE REPORT

Benzyl Chloride (58)

1. GENERAL

Benzyl chloride is a colorless, highly refractive liquid with a very pungent aromatic odor. Its vapors are irritating to the eyes and mucous membranes, and it is classified as a powerful lacrimator. Benzyl chloride is insoluble in cold water, but decomposes in hot water to give benzyl alcohol.[1433]

Benzyl chloride may be commercially produced by several methods. The principal method consists of chlorinating boiling toluene in the absence of light. The reaction mixture is agitated with mild alkali and distilled. It can also be produced in a continuous manner by mixing toluene and chlorine in the vapor phase.[1433]

Commercial facilities for the manufacture of benzyl chloride are operated by Hooker Chemical Company,[1815] Stauffer Chemical Company,[1571] Tenneco Chemicals Incorporated,[1571] and Velsicol Chemical Corporation.[1571]

2. TOXICOLOGY[1495]

Benzyl chloride is an irritant in both its liquid and vapor form. On contact with the skin it can cause redness and irritation. The warning properties of benzyl chloride are tears and coughing which generally result after exposure to concentrations of approximately 16 ppm. After severe vapor exposure, pulmonary edema may occur.

Benzyl chloride, if allowed to remain on the skin, will produce severe irritation comparable to a first degree burn. Contact with the eyes will produce severe immediate damage which may result in loss of sight. Repeated exposure to the vapor can cause tears and burning of the eyes as well as coughing. The maximum average atmospheric concentration for an eight-hour working day without injury to health is one ppm.

3. HEALTH AND SAFETY[1495]

Benzyl chloride presents a moderate fire hazard [flash point is 153 F (c.c.)] and should not be handled at temperatures near its flash point unless it is in a closed system free of air or oxygen.

Unstabilized benzyl chloride readily undergoes a Friedel-Crafts type condensation reaction in the presence of copper, aluminum, iron, zinc, magnesium, tin and various other metals which act as catalysts. The heat and hydrogen chloride which are liberated, further accelerate the reaction and may result in the extremely rapid build-up of dangerous pressures in closed vessels. Stabilized benzyl chloride will also undergo the condensation reaction if the aqueous sodium carbonate stabilizing solution becomes exhausted.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation and Personnel Safety in Dealing with Concentrated Benzyl Chloride[1495]

Benzyl chloride is classified by the Interstate Commerce Commission as a corrosive liquid. As such it must be packed in ICC specified containers when shipped by rail, water or highway and all of the ICC regulations regarding loading, handling, and labeling must be followed.[0278]

Employees handling containers of benzyl chloride should wear personal protective equipment such as chemical safety goggles, gloves and for best protection, clothing made of rubber or other impervious materials to protect the body against splashes.

Persons exposed to concentrations of benzyl chloride vapor above the recommended maximum allowable concentration (one ppm) should be provided with proper respiratory protection.[1495]

Stabilized benzyl chloride should never be bulk stored because of its reactive and corrosive nature. It is suggested that this material be stored in the steel drums in which it is shipped and used as soon as possible.

Anhydrous benzyl chloride may be stored for slightly longer periods than the stabilized form. Although it is usually stored in its nickel and glass shipping containers, it may be bulk stored. The material should be protected from water at all times.

Disposal/Reuse of Waste Benzyl Chloride Streams

A definition of acceptable criteria for the disposal of benzyl chloride must also take into account acceptable criteria for the release of hydrogen chloride and hydrochloric acid to the environment, since recommended disposal methods involve some processes that reduce the benzyl chloride to these materials.

Current techniques utilize incineration and land burial. The recommended maximum concentration of benzyl chloride and hydrogen chloride in effluent streams released to the environment are as follows:

Contaminant and Environment	Maximum Concentration and Point Source Release Rate	Basis of Recommendation
Benzyl chloride released to the atmosphere	0.01 ppm (0.05 mg/M^3)/24 hr.	0.01 TLV
Hydrogen chloride released to the atmosphere	0.05 ppm (0.07 mg/M^3)/24 hr.	0.01 TLV
Hydrochloric acid released to the atmosphere	0.05 ppm (0.02 mg/M^3)/24 hr.	0.01 TLV

5. EVALUATION OF CURRENT AND NEAR FUTURE BENZYL CHLORIDE DISPOSAL PROCESSES

Benzyl chloride is expected to appear primarily as dilute aqueous and organic waste streams and occasionally as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Benzyl Chloride

In the event it becomes necessary to dispose of a significant quantity of concentrated benzyl chloride, two disposal options are available. The first option is to incinerate the material using scrubbers to remove the hydrogen chloride from the effluent gas stream. This is an adequate means of disposal. The second option,[1495] is adding solid sodium carbonate or solid lime to the concentrated benzyl chloride and then burying the material in an approved landfill. Concentrated benzyl chloride should not be washed down the drain or burned in open pits.

Dilute Aqueous Waste

Benzyl chloride is insoluble in cold water, but decomposes in hot water to given benzyl alcohol.[1433] It can also be reacted with caustic to form the alcohol.[1495] It is recommended that aqueous waste containing benzyl chloride be converted to the alcohol and then be subjected to secondary treatment with activated sludge. Incineration with adequate scrubbing of the effluent gas is also an acceptable means of disposal.

Dilute Organic Waste

Dilute organic waste containing benzyl chloride can be adequately disposed of by incineration with proper scrubbing of the effluent gas to remove hydrogen chloride. An alternate method of disposal would be to react the waste with solid sodium carbonate or solid lime followed by burial of the resultant material in an approved landfill.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Benzyl chloride is expected to appear primarily as dilute organic waste and to a much lesser degree as dilute aqueous waste and concentrated waste. It is anticipated that facilities for handling the disposal of these wastes will be located at the manufacturing sites. This material is not judged to be a candidate for National Disposal Sites.

7. REFERENCES

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1571. Schnell Publishing Company, Inc. 1971-72 OPD chemical buyers guide. 59th ed. New York, 1971. 1,584 p.

1815. Personal communication. J. F. Henry, J. F. Henry Chemical Company Inc., to W. P. Kendrick, TRW Systems, June 8, 1972.

1816. Personal communication. H. McClure, Velsicol Chemical Corporation, to W. P. Kendrick, TRW Systems, June 8, 1972.

HAZARDOUS WASTES PROPERTIES
WORKSHEET #58

H. M. Name Benzyl Chloride

IUC Name

Common Names alpha-chlorotoluene[3]

Structural Formula

$C_6H_5CH_2Cl$

Molecular Wt.[1] 126.58 Melting Pt.[1] -43 C Boiling Pt.[1] 179 C

Density (Condensed) 1.1026 @ 18/4 C[1] Density (gas) 4.36[1] @ air = 1

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 22 C[2] 5 mm @ 47.8 C[2] 10 mm @ 60.8 C[2]

Flash Point 140 (cc) F[2] / 165 (o.c.) F[3] Autoignition Temp. 1161 F[1]

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (vol %) Lower 1.1 (in air)[2] Upper

Solubility

Cold Water 0.0033% Hot Water Hydrolyzes Ethanol

Others:

Acid, Base Properties Form HCl[6]

Highly Reactive with Unless stabilized with sodium carbonate solution this compound undergoes a Friedel-Crafts type condensation w/HCl liberation.[3]

Compatible with Glass[3], nickel[3], earthenware[3]

Shipped in Glass and earthenware containers, drums, tank trucks and tank cars[3]

ICC Classification Corrosive liquid Coast Guard Classification

Comments Mfg. by: Hooker Chemical Co.[4]; Stauffer Chemical Co.[5]; Tenneco Chemicals Incorporated[5]; and Velsicol Chemical Corp[5].

References (1) 766 (4) 1815
(2) 1433 (5) 1571
(3) 1495 (6) 1816

Give a reference for each entry.

Supply units where necessary

PROFILE REPORT

Diborane, Tetraborane, Pentaborane-9, Pentaborane-11, Hexaborane and Decaborane (61,505)

1. GENERAL

Structure and Nomenclature

The boranes (boron hydrides) are polymers of boron and hydrogen. The boron atoms are bonded to each other directly and also by means of hydrogen atoms which form bridges between them by means of hydrogen-bonding. Their chemical properties and reactions are well-documented in several comprehensive reviews.[1433,2005,2009,2014,2002] Representative structures have been delineated (Figure 1).[1433] The monomer exists only transistorily. For the boranes which are relatively stable, the number of boron atoms in the compound is denoted by a Greek prefix, e.g., diborane for B_2H_6, tetraborane for B_4H_{10}, etc. If there may be some ambiguity with respect to the number of hydrogen atoms involved, that number is specified in parentheses, e.g., pentaborane (9) for B_5H_9 and pentaborane (11) for B_5H_{11}.

Production

There is only one producer of boranes in the United States, the Callery Chemical Company, Callery, Pennsylvania.[2020] By 1962, Callery had produced 500,000 lb of assorted boranes under government contract for research in rocket fuels. Of this quantity, approximately 200,000 lb of pentaborane (9) remains in storage at Edwards Air Force Base, California, in the Mojave Desert. None is being produced for this purpose at present, nor is any future need anticipated, since its extreme toxicity and thermodynamic properties make it unfavorable with respect to F_2-H_2, F_2-O_2 and other newer formulations.[2019,2020]

Only diborane and decaborane are manufactured at present. There are several viable processes for producing diborane, either commercially or on a laboratory scale (e.g., Figures 2 - 4).[2092] At present, Callery produces diborane only at its Callery, Pennsylvania facility by reacting sodium hydride with methylborate according to the following reactions[2092,2020]:

1) $H_3BO_3 + 4CH_3OH \xrightarrow{\text{distillation}} CH_3OH\cdot(CH_3O)_3B + 3H_2O$ Yield = 98%

2) $CH_3OH\cdot(CH_3O)_3B \xrightarrow{\text{Mineral oil extraction}} (CH_3O)_3B + CH_3OH$ Yield = 96%

3) $2(CH_3O)B + NaH \xrightarrow{\text{in mineral oil}} (OCH_3)_2BH + NaB(OCH_3)_4$ Yield = 94%

4) $6(CH_3O)_2\,BH \xrightarrow{\text{straight disproportionation}} B_2H_6 + 4(CH_3O)_3B$ Yield = 100%

There is essentially no toxic waste generated by the process. Although the producers would not release a production figure, an unidentified source estimated an annual production of <200 lb, which is almost all sold as a 10 mole per cent mixture in either argon, nitrogen or hydrogen at $85/lb contained B_2H_6.

Decaborane is produced by pyrolysis of diborane. Miscellaneous toxic wastes are separated and incinerated. The stack gases are neither monitored nor controlled. Decaborane is of some research interest as a component of solid propellants, and the exact amount produced is classified by the Department of Defense. At $1000/lb, however, it is doubtful if much is produced.

Tetraborane, pentaborane (11), and hexaborane are highly unstable laboratory curiosities which are produced locally in individual research laboratories in negligible quantities. They rapidly transform to the other boranes with the evolution of hydrogen.

Uses

Diborane is used almost exclusively for defect doping in the manufacture of semiconductors. Three major gas suppliers, Matheson Gas Products, Cucamonga, California[2011] and Newark, California,[2010] Air Products and Chemicals Inc., Long Beach, California[2015] and Emmaus, Pennsylvania,[2017] and the Linde Division, Union Carbide Corporation, Torrance, California,[2018] buy 10 mole percent B_2H_6 mixed with either argon, nitrogen, or hydrogen at $85/lb contained B_2H_6, further dilute it to various concentrations from 10 ppm to 1000 ppm (but most typically 100 ppm), and resell it to the semiconductor manufacturers, who use it to introduce defects in the assembly line production of semiconductors, at temperatures ranging from moderate to 1100 C. Two manufacturers, TRW Semiconductors, Lawndale, California[2016] and Collins Radio Company, Newport Beach, California[2012] report annual use of 10 and 6 standard 240 ft^3 cylinders of diluted gas, respectively.

Aside from a small amount of decaborane used in classified research in solid propellants, 20 to 30 kg/yr are used by the Olin Corporation, New Haven, Connecticut, in the manufacture of Dexsil, a patented, polysilicone, high temperature elastomer.[2008] The decaborane is obtained at present from a large stockpile which is the property of Olin. Since the material is very valuable at $1000/lb on the open market, all waste is recycled and one escapes. The stockpile is stored at cryogenic temperatures and is continuously monitored for the evolution of hydrogen, which would signal that decomposition is occurring.

On the West Coast, Chemical Systems, Inc., Santa Ana, California,[2006] manufactures Pentasil, which is similar to Dexsil, but uses pentaborane instead. They use 50 to 75 lb/yr of pentaborane, which they obtain from the stockpile at Edwards Air Force Base, California. Their only waste product is hydrogen, which is vented. Occasionally, they experiment with diborane, which is reacted completely with acetylene in a bomb to produce boron carbide and hydrogen.

2. TOXICOLOGY[0766,0648,2000,1312,2092]

Health and Safety Standards

Recommended Threshold Limit Values (TLV) have been established by the American Conference of Governmental Industrial Hygienists for diborane, pentaborane (9), and decaborane, as follows:

	Threshold Limit Value	Minimum Level Detectable by Odor by Man[648]
Diborane	0.1 ppm (100μg/m^3)	3.3 ppm (33,000μg/m^3)
Pentaborane	0.005 ppm (10μg/m^3)	0.8 ppm (1,600μg/m^3)
Decaborane	0.05 ppm (300μg/m^3)	0.7 ppm (4,200μg/m^3)

It is seen that the minimum concentrations detectable by odor are much higher than the maximum set for reasons of health. Consequently, odor may not be relied upon as a means of detection. While several instruments are available for the detection of boranes in the sub-parts per million range,[2092] they are of limited utility due to non-portability and/or non-specificity. Detection remains as an outstanding problem.

The Committee on Toxicology of the National Research Council has established Emergency Exposure Limits (EEL) for diborane as 10 ppm for 10 minutes, 5 ppm for 30 minutes, and 2 ppm for 60 minutes.[2092] These are not safety limits, but rather predictions for the onset of clinical symptoms without incapacitation. Similarly, an EEL of 25 ppm for 5 minutes has been set by the American Industrial Hygiene Association for pentaborane.[0648]

Epidemiology

Accidents involving human exposure to boranes have primarily involved inhalation and subsequent lung irritation and pulmonary edema. Attack of the central nervous system has been inferred by accompanying listlessness, incoordination, and similar symptoms. This clinical evidence has been supplemented by laboratory experiments with dogs and rats, which have produced liver and kidney damage in addition.[0766,0648] It has not been determined whether the effects of borane poisoning are cumulative in animals or man. The 1971 Annual List of Toxic Substances[1312] reports 50th percentile lethal doses or lethal concentrations (LD50 or LC50) as:

Diborane	80 ppm LC50 in the rat by inhalation.
Pentaborane	0.72 mg/kg LD50 in man by inhalation.
	7 ppm LD50 in the rat by inhalation
	11.1 mg/kg LD50 in the rat administered intraperitoneally.
Decaborane	230 mg/m^3 LC50 in the rat by inhalation
	64 mg/m^3 LD50 in the rat administered orally.

3. OTHER HAZARDS

Pure boranes are stable. However, small quantities of wide varieties of impurities, particularly oxidizing substances, water, or halogenated hydrocarbons, renders them extremely unstable with respect to thermal or mechanical shock.[2092,2000] This could account for wide discrepancies in experimental results on the pyrophoricity of diborane. It must always be assumed in the absence of a great preponderance of evidence to the contrary that a borane cylinder is so contaminated. The problem is compounded by the likely evolution of hydrogen gas on reaction, decomposition or polymerization, or testing. The hydrogen, itself, is of course, highly explosive, and can cause cylinders to burst by pressure build-up. At slightly elevated temperatures, diborane will decompose (or polymerize) to release varying amounts of hydrogen. Alternatively, the high polymers will decompose, also releasing hydrogen. Some of the rates of the reactions have been investigated as a function of time and temperature (Figure 5).[1414]

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage and Transportation

Procedures for the handling, storage and transportation of boranes are well-documented.[2000,2092] Monitoring is complicated somewhat by the lack of convenient, specific detection apparatus, but since leakage is invariably accompanied by decomposition or polymerization with an accompanying evolution of hydrogen, the chemical and physical characteristics of a batch can be fairly easily determined by a search for hydrogen gas. The 200,000 lb of pentaboranes stored at Edwards Air Force Base, California is periodically inspected by civilian and military personnel for corrosion of the cylinder valves.[2007]

Only the three most stable boranes -- diborane, pentaborane(9), and decaborane -- are shipped in any quantity. It is preferred, but not required, that they be stored and shipped at cryogenic temperatures. In any case, space should be available for possible hydrogen evolution within the container. Interstate Commerce Commission Regulations[0278] makes no special material provisions for shipping containers, other than the general specifications for gases. Other specific requirements are:

Diborane	Special permit required.
Pentaborane (9)	Not acceptable for rail shipment.
Decaborane	25 lb maximum container.

Disposal and Reuse

Diborane: There is no generation of diborane or other hazardous waste in the production of diborane by the Callery Chemical Company. Waste is generated, however, when the 10 mole percent gas is diluted by Matheson, Air Products and Chemicals, or Linde, respectively. This waste is in the form of residual gas remaining in the manifolds after mixing is complete.

Air Products and Chemicals Inc. mixes diborane with H_2, N_2 or argon in three locations in the United States - Emmaus, Pennsylvania,[2017] Long Beach, California,[2015] and Houston, Texas. The Emmaus, Pennsylvania facility runs about 0.1 ft^3 every six months to a storage cylinder, which has been filling for six years and is currently half full. They are not concerned at present with disposal of this cylinder approximately six years hence. Used cylinders are returned to Callery, where they are probably burned. The Long Beach, California facility handles approximately 10 lb/yr of the 10 mole percent mixture. They occasionally vent "a few cc of the mixture" to the atmosphere with no monitoring or control.

Used return cylinders are burned with no control. The Houston facility operates similarly to the Long Beach facility.

The Linde Division of the Union Carbide Corporation mixes diborane in five locations - East Chicago, Indiana; Houston, Texas; Keaseby, New Jersey; Linden, New Jersey; and Torrance, California.[2018] The Torrance, California facility uses approximately 60 lb/yr of the 10 mole per cent mixture. After dilution there is usually a residual of 500 cc, which is disposed of either by: 1) transferring it into a garbage cylinder and dumping the cylinder; 2) diluting with N_2 and venting to the atmosphere; 3) scrubbing with water and sewering; or 4) bubbling through 5 gal alcohol and venting the exhaust gases to the atmosphere in an uncontrolled manner. They claim never to have detected boron-containing compounds in the atmosphere.

Matheson Gas Products mixes diborane in three locations - Cucamonga, California,[2011] Newark, California,[2010] and East Rutherford, New Jersey. The East Rutherford facility burns all waste and vents the B_2O_3 particulate-laden waste to the atmosphere in an uncontrolled manner. The Cucamonga facility evacuates most of its waste into a garbage cylinder which is shipped to Newark for disposal. Some waste at Cucamonga is absorbed in aqueous ammonia. The resultant boric acid suspension is then sewered in compliance with local water district regulations, which specify a maximum 500 ppm suspended solids. The Newark facility absorbs all diborane waste in aqueous ammonia and meters it into the sewer system under regulations which specify a pH range of 6.4 to 7.8. No analysis is made of the effluent for the concentration of boron or boron-containing compounds.

Two typical semiconductor manufacturers were contacted--TRW Semiconductors, Lawndale, California,[2016] and Collins Radio Company, Newport Beach, California.[2012] In the TRW process, the B_2H_6 is completely reacted to B_2O_3 at 1100 C. Some is vented; the major portion, amounting to 0.2 g/mo, is sewered. In the Collins process, the exhaust gases containing B_2H_6 and B_2O_3 are scrubbed with water. The effluent is neutralized with NH_3, and returned to the sanitary water supply. A slight deposit has been accumulating over a period of time in the bottom of the neutralizing tank, which "is of no concern at present. It has never been chemically analyzed."[2012]

Pentaborane (9): The use of 50 to 75 lb/yr of pentaborane by Chemical Systems Inc., Santa Ana, California[2006] in the manufacture of their high temperature elastomer, Pentasil, generates no waste except H_2, which is vented. At Edwards Air Force Base, California[2007] periodic inspections of the 200,000 lb stockpile occasionally reveal a cylinder with a corroding valve, although none has been found in the past two years. Damaged cylinders are trucked to remote portions of the Mojave Desert, where they are exploded by machine gun fire.

Decaborane: The high value of decaborane causes the Olin Corporation[2008] to recycle all decaborane waste in the production of its high temperature elastomer, Dexsil. Consequently, there is no waste released to the environment. Its stockpile of decaborane is stored at cryogenic temperatures and is monitored for the evolution of hydrogen, which would signal decomposition.

The manufacture of decaborane by the Callery Chemical Company[2020] creates solid, toxic wastes, which are burned in an uncontrolled manner. No information is available on the ultimate disposition of decaborane used in classified research on solid propellants.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No.1 - Venting to the Atmosphere

This is the procedure used by many of the gas mixing plants for the disposal of residual diborane. Since the TLV for diborane is so stringent (0.1 ppm, corresponding to $100 \mu g/m^3$), it is doubtful if this limit is being met consistently. There is certainly no evidence for compliance. Attempts to obtain evidence are hindered by the lack of suitable detection equipment which is both portable and specific.[2092]

Option No.2 - Destruction by Burning or Explosion and Venting of Exhaust Products

This procedure is superior to simple venting, since the resultant particulate B_2O_3 is less hazardous than any of the boranes themselves. Here again, though, there is no evidence that the release of the B_2O_3 is being kept within safe limits. The gas-mixing plants which employ this procedure for the disposal of residual diborane and the Callery Chemical Company, which burns the toxic wastes resulting from the production of decaborane, are located in heavily populated areas, and the lack of information with regard to the B_2O_3 released is of concern. On the other hand, the disposal of occasional cylinders of pentaborane (9) by this method in isolated areas of the Mojave Desert is satisfactory. There is little concern for B_2O_3 leaching into any ground water, since the high-fired form is essentially insoluble.

Option No.3 - Wet Scrubbing and Sewering

The instability of boranes when in contact with water, particularly aqueous ammonia, is of great advantage, since hydrolysis occurs easily and goes quickly to completion. The outstanding concern, however, is the possible release of undesirable amounts of boric acid solution and low-fired B_2O_3 aqueous suspension to the environment.

6. CONCLUSIONS, RECOMMENDATIONS AND SUITABILITY FOR NATIONAL DISPOSAL SITES

Boranes have low threshold limit values, are very difficult to detect, and appear as problem wastes in relatively few locations in relatively small volumes. As such, they are ideal candidates for National Disposal Sites. Also, there are no undue restrictions on shipment, so transport to National Disposal Sites will not prove difficult.

The current practices of venting boranes and their combustion and solution products (boric oxide and boric acid) must be regarded as unsatisfactory. No attempts are made to monitor air and water emissions.

The relatively low volume of material and the technical difficulty of monitoring boron and its compounds would make routine analysis difficult and expensive for the gas mixing plants.

Since the waste diborane is already in a gastight system under high pressure, it would be relatively easy to evacuate it into a garbage cylinder for eventual shipment to a National Disposal Site. Similar procedures are already practiced by the Matheson Cucamonga plant when it ships its wastes to the Newark plant and by the Air Products Emmaus plant as it stores its waste indefinitely in its giant garbage cylinder. Similarly, the Callery Chemical Company would no doubt find it more convenient to ship its solid wastes from decaborane production to someone else, rather than burn them on its own property. Thus, the release of all boranes to the environment would essentially cease with great benefit to all.

At the National Disposal Site, the borane wastes could either be burned and the exhaust gases scrubbed to remove the B_2O_3 particulates, or the wastes could be hydrolyzed with subsequent evaporation to solid boric acid. In either case, the borane wastes would be reduced to a low volume of relatively nonreactive, non-toxic solids. If the disposal site is sufficiently isolated, even the scrubbing and/or hydrolysis could be waived with a high margin of safety.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 61

IUC Name Diborane

Common Names Boron hydride, boroethane

Structural Formula

B_2H_6

Molecular Wt.[1] 27.7 Melting Pt.[2] -165.5 C Boiling Pt. -9.25 C

Density (Condensed) 0.577 @ -183 C Density (gas) ____ @ ____ ° ____

Vapor Pressure (recommended 55 C and 20 C)

22 mm @ -112 C ____ @ ____ ° ____ @ ____ °

Flash Point -130 F Autoignition Temp. 100 -125 F

Flammability Limits in Air (wt %) Lower <0.9% Upper >98%

Explosive Limits in Air (wt. %) Lower 0.9% Upper 98%

Solubility

Cold Water dissociates Hot Water dissociates Ethanol ____

Others: NH_4OH

Acid, Base Properties slightly acidic

Highly Reactive with water or steam to produce H_2; reacts explosively with oxidizing materials; rubber, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in mild steel gas cylinders

ICC Classification flam-compressed gas, red label Coast Guard Classification ____

Comments Special Permit required.

References (1)
(2)
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 61

IUC Name Tetraborane

Common Names Dihydrotetraborane, boron hydride, borobutane
tetraborondecahydride

Structural Formula

B_4H_{10}

Molecular Wt.[1] 53.4 Melting Pt.[2] -120 C Boiling Pt. 18 C

Density (Condensed) 0.59 @ -70 C Density (gas) 1.8 @ 6 ° C

Vapor Pressure (recommended 55 C and 20 C)

580 mm @ 6 C @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hydrolyzes Hot Water Hydrolyzes Ethanol Dissociates

Others: Benzene

Acid, Base Properties slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with Stainless steel, most metals, asbestos, graphite

Shipped in not shipped

ICC Classification Coast Guard Classification

Comments

References (1)
(2)
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 61,505

IUC Name Pentaborane (9)

Common Names Pentaboron enneahydride, pentaborane (stable), boron hydride

Structural Formula

B_5H_9

Molecular Wt.[1] 63.2 Melting Pt.[2] -46.6 C Boiling Pt. 58.4 C

Density (Condensed) 0.61 @ 0 C Density (gas) 2.2 @ 0 ° C

Vapor Pressure (recommended 55 C and 20 C)

66 mm @ 0 C ____ @ ____ ° ____ @ ____ °

Flash Point 30 C Autoignition Temp. 35 C

Flammability Limits in Air (wt %) Lower Spontaneously flam Upper ____

Explosive Limits in Air (wt. %) Lower 0.42% Upper ____

Solubility

Cold Water Hydrolyzes Hot Water Hydrolyzes Ethanol ____

Others: ____

Acid, Base Properties Slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in mild steel gas cylinders

ICC Classification flam.liquid, red label Coast Guard Classification flam.liquid, red label

Comments Not acceptable by rail, Code of Federal regulations Sec. 73.138 MCA warning label

References (1)

(2)

(3)

[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 61

IUC Name Pentaborane (11)

Common Names Dihydropentaborane, pentaborane (unstable), boron hydride

Structural Formula

B_5H_{11}

Molecular Wt.[1] 65.2 Melting Pt.[2] -123 C Boiling Pt. 63 C

Density (Condensed) ____ @ ____ ° ____ Density (gas) ____ @ ____ ° ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ° ____ @ ____ ° ____ @ ____ °

Flash Point ____ ° Autoignition Temp. ____ °

Flammability Limits in Air (wt %) Lower Spontaneously flam. Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water Hydrolyzes Hot Water Hydrolyzes Ethanol ____

Others: ____

Acid, Base Properties Slightly acidic.

Highly Reactive with Oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in Not shipped

ICC Classification flam. liquid, red label, not acceptable. Coast Guard Classification ____

Comments ____

References (1)

(2)

(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 61

IUC Name Hexaborane

Common Names Boron hydride, hexaboron decahydride

Structural Formula

B_6H_{10}

Molecular Wt.[1] 75.0 Melting Pt.[2] -65.1 C Boiling Pt. 0 C @ 7.2 mm

Density (Condensed) 0.69 @ 0 C Density (gas) 2.6 @ 0 C

Vapor Pressure (recommended 55 C and 20 C)

7.2 mm @ 0 C ____ @ ____ ° ____ @ ____ °

Flash Point ____ ° Autoignition Temp. ____ °

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water Hydrolyzes Hot Water Hydrolyzes Ethanol ____

Others: ____

Acid, Base Properties Slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in Not shipped

ICC Classification ____ Coast Guard Classification ____

Comments ____

References (1)
(2)
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 61

IUC Name Decaborane

Common Names Boron hydride, decaboron tetradecahydride

Structural Formula

$B_{10}H_{14}$

Molecular Wt.[1] 122.3 Melting Pt.[2] 99.7 C Boiling Pt. 213 C

Density (Condensed) 0.94 @ 20 C Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

19 mm @ 100 C 66 mm @ 132 C @ °

Flash Point 80 C Autoignition Temp. 149 C

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Slightly Hot Water Dissociates Ethanol Yes

Others: CS_2, ether, benzene

Acid, Base Properties Slightly acidic

Highly Reactive with oxidizing materials, water or steam, rubbers, greases, halogenated hydrocarbons

Compatible with stainless steel, most metals, asbestos, graphite

Shipped in mild steel barrels or drums

ICC Classification flam.solid, yellow label,25lb Coast Guard Classification

Comments Code of Federal Regulations Sec. 73.236

References (1)

(2)

(3)

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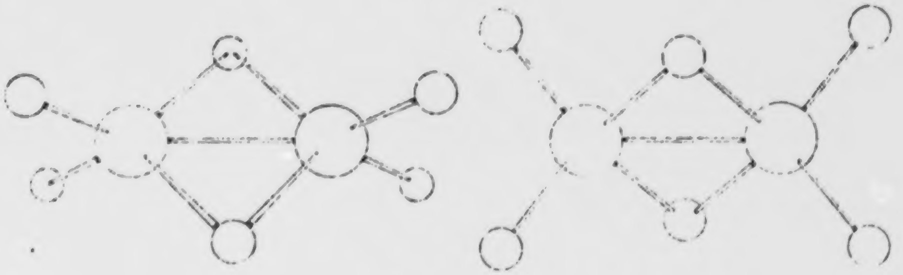
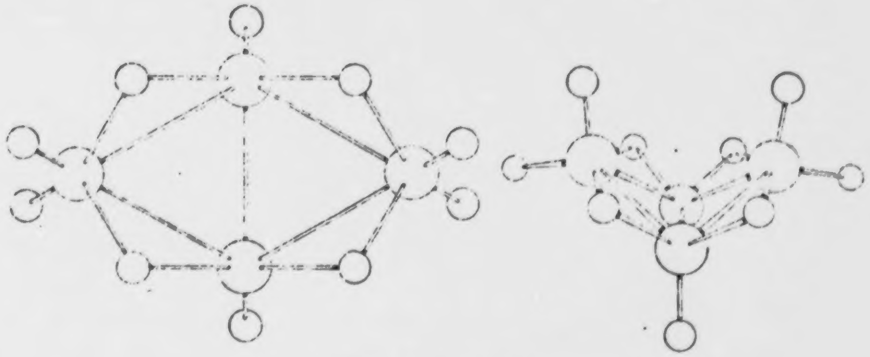
[1] Give a reference for each entry.

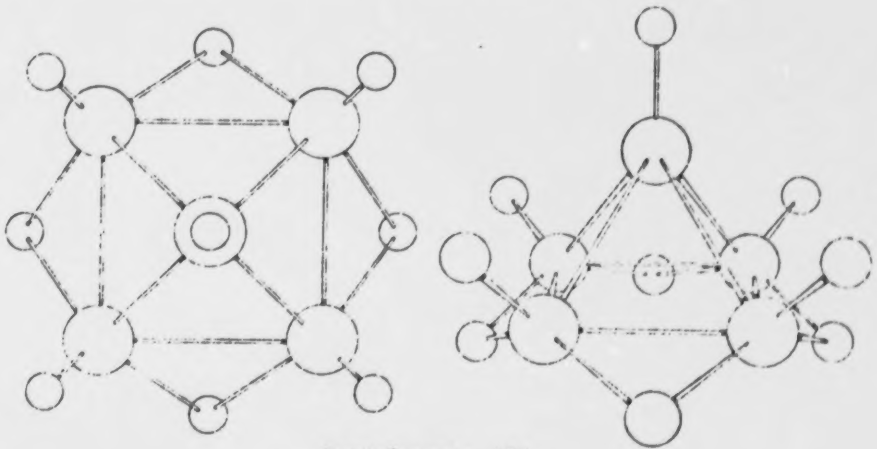
[2] Supply units where necessary



Diborane

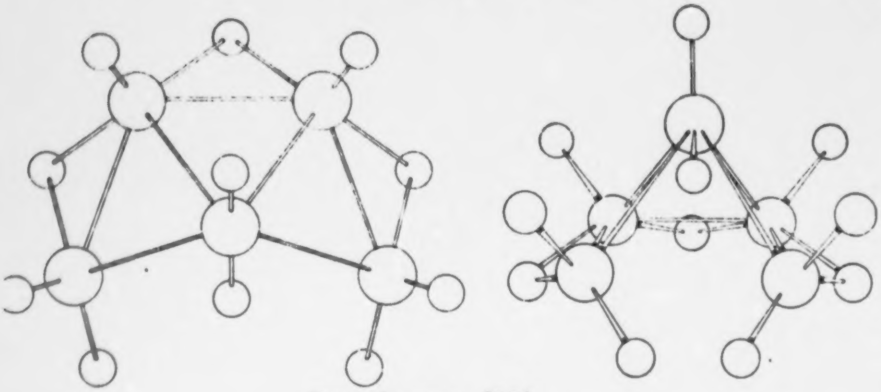


Tetraborane (10)



Pentaborane (9)

Figure 1.[1433] Representative structures of some Boranes.



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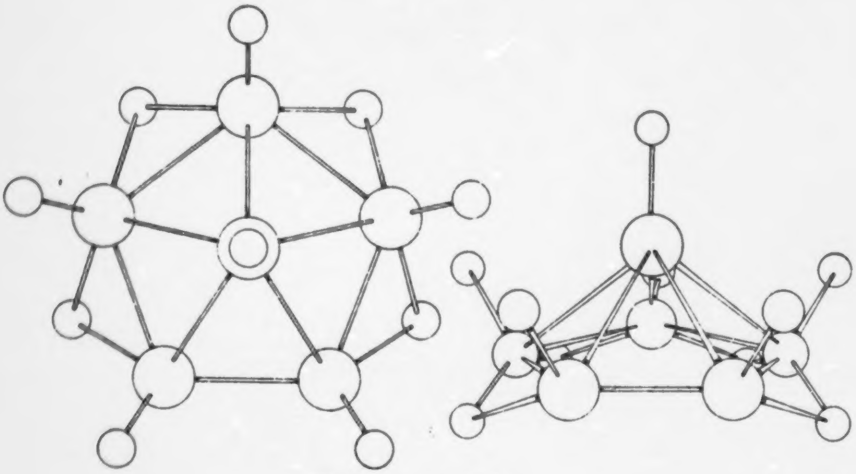
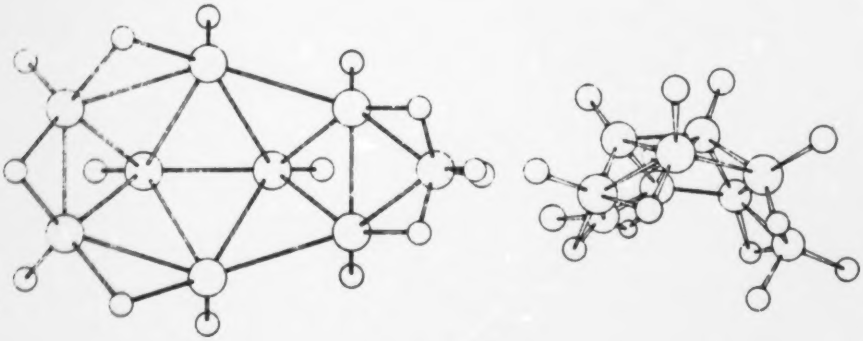


Hexaborane(10)



Nonaborane (15)

Figure 1. (Continued)

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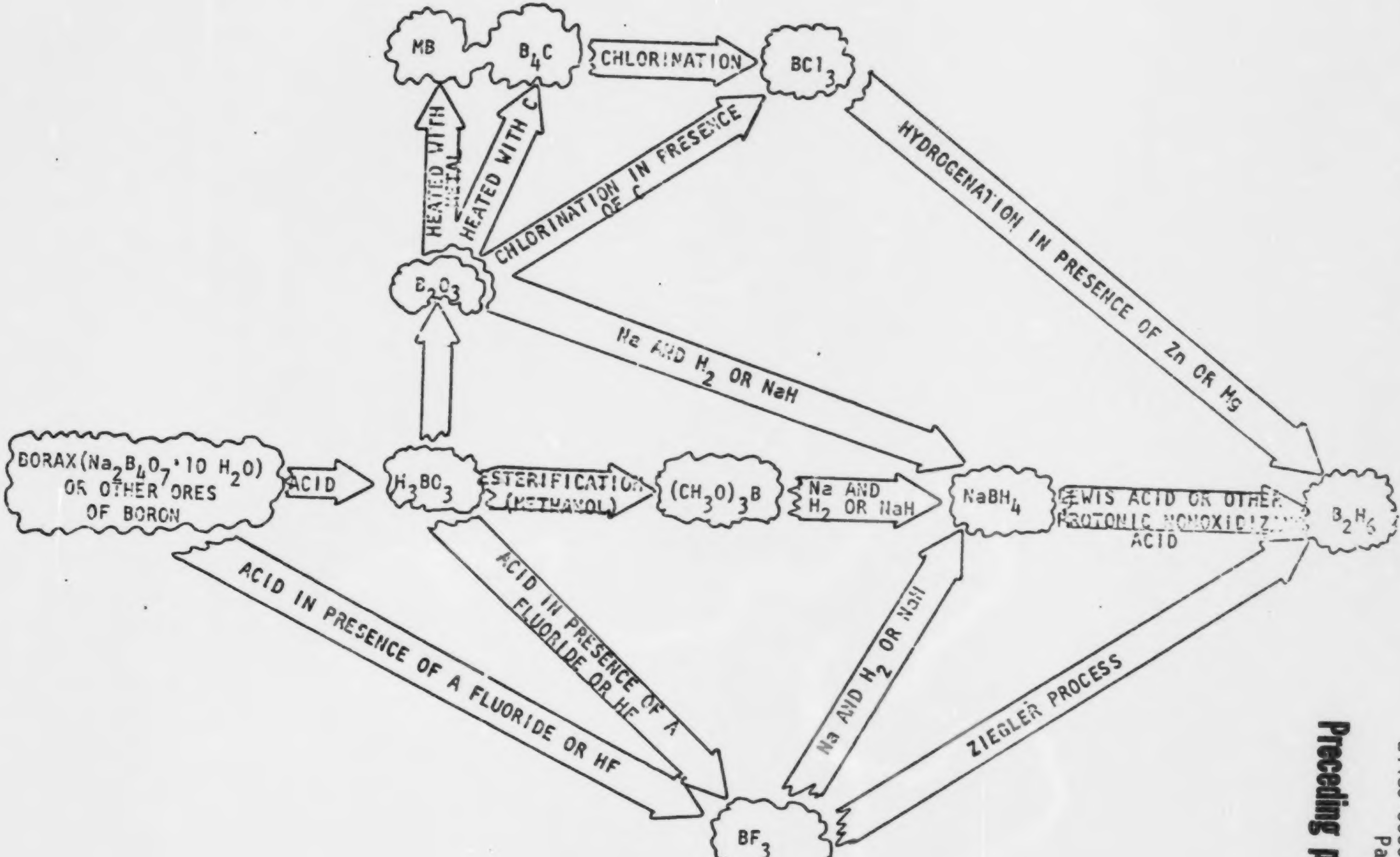
MB
B4C
CHLORINATION
BCl3
HEATED WITH METAL
HEATED WITH C
CHLORINATION IN PRESENCE OF C
HYDROGENATION IN PRESENCE OF Zn OR Mg
B2O3
Na AND H2 OR NaH
BORAX(Na2B4O7·10 H2O) OR OTHER ORES OF BORON
ACID
H3BO3
ESTERIFICATION (METHANOL)
(CH3O)3B
Na AND H2 OR NaH
NaBH4
LEWIS ACID OR OTHER PROTONIC NONOXIDIZING ACID
B2H6
ACID IN PRESENCE OF A FLUORIDE OR HF
ACID IN PRESENCE OF A FLUORIDE OR HF
Na AND H2 OR NaH
ZIEGLER PROCESS
BF3

Figure 2.[2092] Flow Chart for the Preparation of Diborane via the Conversion of Boron Ores Into Boron Halides or Sodium Borohydride.

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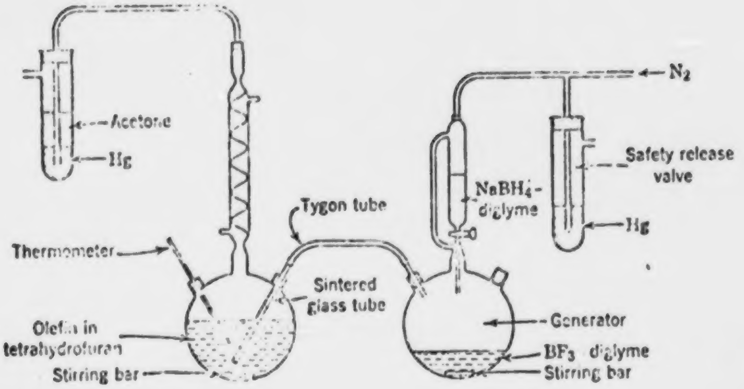
Acetone
Hg
Thermometer
Tygon tube
Sintered glass tube
Olefin in tetrahydrofuran
Stirring bar
N_2
Safety release valve
$NaBH_4$-diglyme
Hg
Generator
BF_3 diglyme
Stirring bar

Figure 3. Laboratory Method for the Preparation of Diborane[2092]

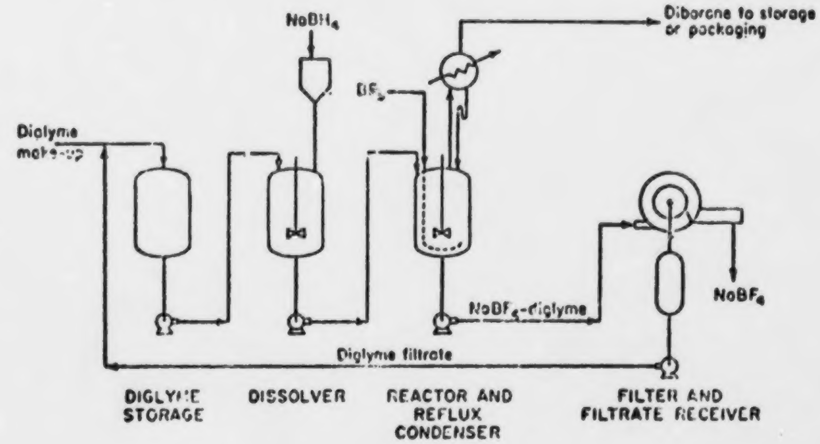
$NaBH_4$
Diborane to storage or packaging
BF_3
Diglyme make-up
$NaBF_4$
$NaBF_4$-diglyme
Diglyme filtrate
DIGLYME STORAGE
DISSOLVER
REACTOR AND REFLUX CONDENSER
FILTER AND FILTRATE RECEIVER

Figure 4. Flow Diagram for the Commercial Manufacture of Diborane by the $NaBH_4$-BF_3-Diglyme Process[2092]

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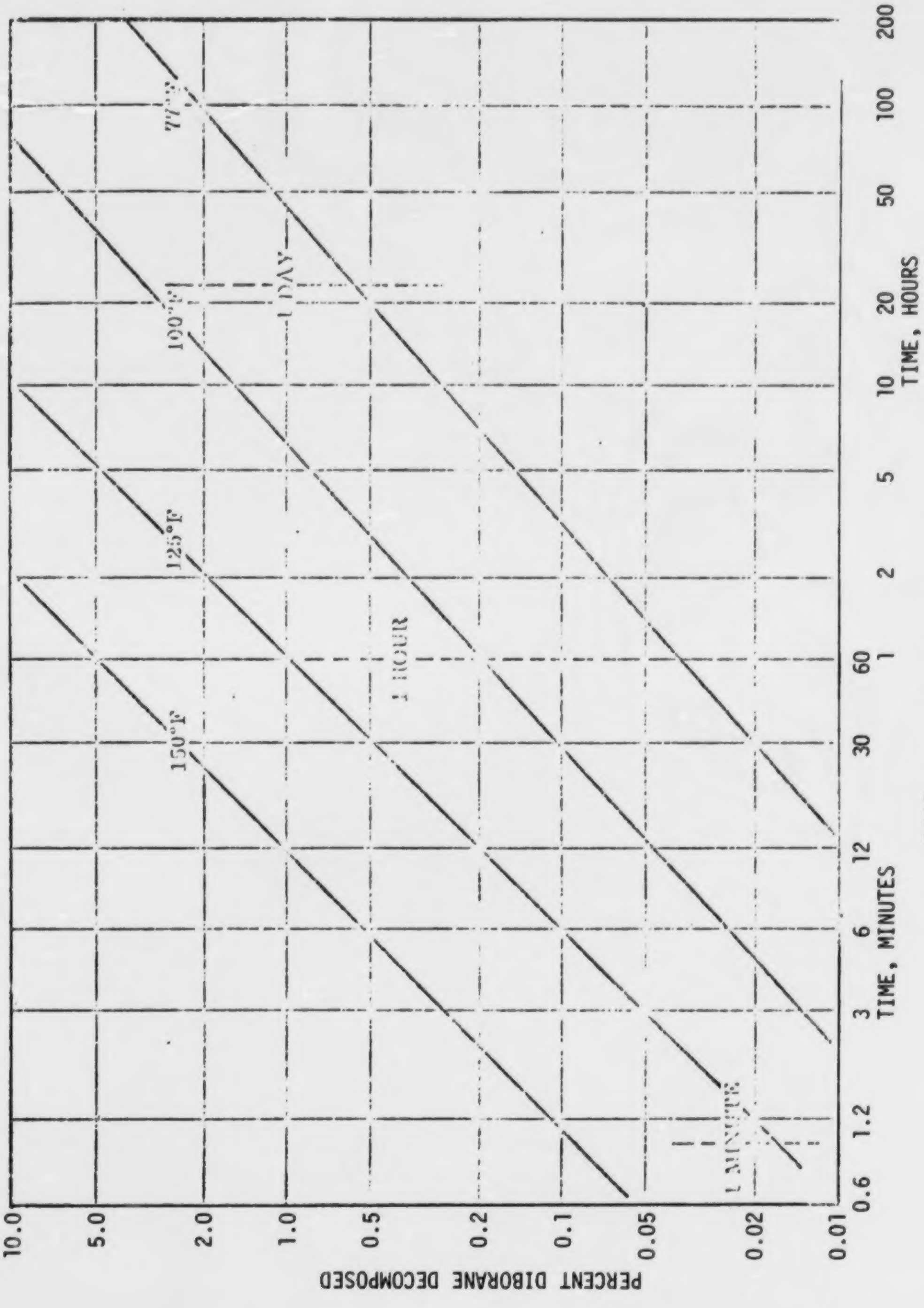

Figure 5.[1414] Diborane Decomposition

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PROFILE REPORT ON ARSENITES

Calcium Arsenite (88), Sodium Arsenite (377), Copper Acetoarsenite (490), Lead Arsenite (236), Potassium Arsenite (341), and Zinc Arsenite (454)

1. GENERAL

The arsenite compounds are characterized as having the AsO_2 or AsO_3 radical in contrast to the AsO_4 radical of the arsenates. Only two of them are believed to have significant commercial consumption in the United States. Sodium arsenite is used as a poison in baits, a corrosion inhibitor, and a weed killer, while copper acetoarsenite, commonly known as Paris Green, finds general use as an insecticide. The other four arsenite compounds are not being used in significant amounts by any commercial or industrial interests.[1711, 1763] Furthermore, it is difficult to even determine where to purchase these chemicals, a fact that is detailed later. For these reasons, the emphasis of this profile report will be directed towards the two compounds that have commercial significance in industry or agriculture and which could possibly occur as wastes from their use or unwanted byproduct manufacture. The profile report will also present what pertinent information has been available on the remaining compounds.

Copper Acetoarsenite

Paris Green is the common name for copper acetoarsenite $[(CH_3CO_2)_2Cu \cdot 3Cu(AsO_2)_3]$. In the late 19th century, it was a very common insecticide. It is useful against the potato beetle, the codling moth, and canker worms. It has some inherent disadvantages however, which include the tendency to burn foliage, rapid settling from suspensions and poor adhesive qualities. It has been virtually replaced by lead arsenate and organic pesticides, and is seldom used as an insecticide on crop plants. It is, however, finding considerable use as a larvicide to control mosquitoes.[1742] Paris Green is also employed for the control of dry wood termites by injection, in solid form, into holes drilled in infested timbers. Production is at least 100,000 lbs per year.[1785]

It is widely believed that Paris Green and its homologs are complex compounds of copper metaarsenite and the copper salt of acetic acid. The ratio of the two constituents is normally very close to 3:1. Paris Green is manufactured commercially by reacting sodium arsenite (prepared from white arsenic and caustic soda) with copper carbonate and acetic acid. Production is by means of a batch process. The reaction continues until the insoluble, green product precipitates from the solution. A complete reaction is indicated by a water white supernatant which contains only soda.[1785] This supernatant solution, said to be arsenic free, is dumped.

After application on crops, Paris Green breaks down rather rapidly. Decomposition through hydrolysis results in the formation of soluble arsenic compounds. This undesirable tendency to hydrolyze into soluble arsenic compounds, in addition to the commercial product containing additional soluble arsenic compounds prevents the use of Paris Green on plants which are not highly resistant to the elements.[1742]

Sodium Arsenite

The common name sodium arsenite is given to a group of several compounds that are used as insecticides in baits and as herbicides for highway and railroad right-of-way weed control. These compounds probably consist mainly of either sodium orthoarsenite (Na_3AsO_3), sodium metaarsenite ($NaAsO_2$),or a combination of the two. This compound is always sold commercially in liquid form. It is manufactured by dissolving arsenic trioxide in liquid caustic soda. The sodium arsenite solution is filtered before drumming and the filter cake resulting from the filtration is buried in public dumps.[1740] The composition of the waste filter cake was not available and the public dump accepting these materials was not identified. A typical, commercial sodium arsenite solution contains four to six pounds of sodium arsenite per gallon of solution. Other uses for sodium arsenite solutions include treatment of certain plant diseases especially on grapes, subterranean termites, and a cattle, goat and sheep dip.[1728]

As well as can be determined, only two companies remain as major manufacturers of sodium arsenite. They are Chevron Chemical Corporation, and Los Angeles Chemical Company. Chevron Chemical Corporation markets a

42 percent sodium arsenite product under the name of W-41 Corrosion Inhibitor and Sodite Grape Spray, as well as a 55 percent arsenite product called Arsenical Weed Killer. Production of the sodium arsenite solutions from Chevron Chemical Company and Los Angeles Chemical Co. are believed to be 200,000-400,000 gallons per year on a 4 to 6 lb per gallon basis. Sodium arsenite is shipped in steel drums, the maximum size being 55 gallons. It is classified by DOT as a Class B poison.

Other Arsenite Compounds

Very little information is available to define the properties, production methods, uses and the consumption of the other arsenite compounds that require discussion in this profile report. Lead arsenite and zinc arsenite are not listed in the three major important reference works on commercially available chemicals.[1571,1670,1790] Calcium and potassium arsenite were mentioned only in one of the three sources. This would indicate that these four arsenite compounds have a very small consumption within the United States. The following paragraphs present these four compounds and discuss what little information on them that was available.

Calcium arsenite ($CaHAsO_3$) is also known as monocalcium arsenite and is a white powder of varying composition which has high toxicity.[1742] It is classified as a Class B poison by the DOT, and can be used as an insecticide and germicide. No other uses were found outside agriculture.[1492]

There are two lead arsenite compounds which are included in the scope of this profile report. The first is lead mataarsenite which has the formula $Pb(AsO_2)_2$. It is insoluble in water and its only listed use is an insecticide.[1742] It is classified as a Class B poison by DOT and it emits toxic fumes on heating.[0766] The other lead arsenite compound is that of lead orthoarsenite, $Pb_3(AsO_3)_2 \cdot XH_2O$. Generally, it has similar physical and toxic properties as the metaarsenite compound and its only known use is also as an insecticide.

There are two potassium arsenite compounds having properties suitable for commercial use. The first is potassium metaarsenite ($KAsO_2$). It is soluble in water and is considered very poisonous, the LD_{50} for rats, orally, being 14 mg/kg.[1492] It is considered as a Class B poison by DOT. No reference describing potassium arsenite being useful as a pesticide was found. It was used in the manufacture of mirrors by reducing silver salts to metallic silver, and was, at one time, used in solution for medicinal purposes.[1492] The other potassium arsenite compound is potassium orthoarsenite, K_3AsO_3. It also is very soluble in water and is classified as a Class B poison by DOT. It is doubtful if any arsenicals are being used in medicine today.[1433] It was also determined that experts in mirror plating technology had no knowledge of potassium arsenite currently being used in the plating of mirrors. They indicated that the process would probably be legally banned if not already obsolete.[1769] Thus, there is no evidence of potassium arsenite being used in commercial enterprise.

Zinc arsenite, $[Zn(AsO_2)_2]$ is also known as zinc metaarsenite (ZMA). It is characterized by its low solubility in water and a toxicity that is similar to calcium arsenate.[1742] It is classified as a Class B poison by the DOT and has been used as an insecticide and a wood preservative.[0766]

Market Trends for Arsenites

The arsenical pesticide market has been in broad decline in recent years as a result of the strict government controls placed on them. These materials are highly poisonous in all forms and prolonged application of these and other arsenicals has caused a serious problem of arsenic buildup in the soil. There also is the threat of arsenic being leached out of the soil into streams and rivers where serious damage can occur to the aquatic life.

It is believed that the use of arsenicals will remain at approximately the same levels or may further decrease. Production of the materials will, of course, decrease as demand falls. Thus a large excess of unuseable arsenite compounds is not expected to occur.

2. TOXICOLOGY

Human Toxicity

The arsenite compounds are highly toxic materials and are very dangerous even in low concentrations.[0766] The American Conference of Governmental Hygienists has recommended a threshold limit value of 0.5 milligrams/meter^3

for all arsenic compounds.[0225] This value represents the conditions to which nearly all workers may be repeatedly exposed without adverse effect.

Acute arsenic poisoning from ingestion results in irritation of the stomach and intestines with accompanying nausea, vomiting and diarrhea. In severe cases, collapse and shock can occur with a weak, rapid pulse, cold sweats, coma or death. The diagnosis of latent chronic arsenic poisoning is difficult since the condition may manifest itself with many different and unpredictable symptoms. Included are disturbances of the digestive tract, liver damage resulting in jaundice, blood and kidney disturbances and a variety of skin abnormalties.[0766]

Toxicity Towards Plant and Animal Life

Sodium arsenite is a strong herbicide while Paris Green harms all but a very few types of plants. Thus they are generally considered toxic towards plant life. No plant toxicity information was available on the other four arsenite compounds but it is considered wise to handle those materials as if they were toxic towards plants. The extreme toxicity of these compounds towards human life can be considered the same for animal life as well. All precautions must be taken to prevent leaching from areas of application into streams and rivers where the arsenic compounds can adversely affect aquatic plant and animal life.

Emphasis has so far been placed on the arsenic constituent of the arsenite compounds being discussed but it should not be forgotton that some of the cations involved in these compounds also have toxic properties. The cations of copper, lead and zinc are, under general conditions, also very hazardous toward animal life. Therefore the toxicity of these cations should at least be considered in the scope of this profile report inasmuch as they can render the appropriate arsenites even more toxic. The TLV's of these cations exclusive of arsenic are 1 mg/m^3 and less.[0225]

3. OTHER HAZARDS

The arsenites do not exhibit any explosive,flammable,or volatile properties nor do they present any other hazards.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

The arsenite pesticides require special consideration on their storage, handling, transportation and disposal. Storage areas for these compounds should be isolated from locations where food and animal feed are stored. The solid arsenite compounds should be stored in the containers originally packed by the manufacturer. The use of protective clothing, goggles, gloves and dust filtering respirators are recommended for unloading or otherwise handling these pesticides. Similar precautions are recommended for handling any liquid solutions. Spills of the solid materials should be cleaned up using a vacuum cleaner after a fine spray of water has been laid down to prevent dust. The liquid compounds or formulations should be handled in an area such that if they are spilled they can be contained for easy clean up or transfer to a sump where they will not create a hazard if they are absorbed by the ground.

The arsenite compounds are labeled as Class B poisons and require that all other DOT and ICC regulations should be followed when shipping, storing, or otherwise handling them.

Disposal/Reuse of Arsenite Compounds

The wholesale disposal of arsenite compounds into the air, water, or soil must be considered completely unacceptable considering their high toxicities. The U.S. Public Health Service has established a maximum of 0.05 mg/l arsenic content (50 ppb) for drinking water if no other drinking water is available. The ideal maximum is 0.01 mg/l (10 ppb). Thus aqueous discharges containing 0.01 mg As/l are considered acceptable but it is doubtful that any industry with a significant As discharge can effectively reduce it to the 0.01 mg/l level. There are no official acceptable levels of disposal into the air, or into soil that is not meant to be sterilized, but common sense dictates a zero discharge level. This is a result of the undesirable properties of the arsenicals which cause them to settle out of the air and accumulate in the soil to hazardous proportions. This soil build-up is the central problem arising from the use of the arsenites and is the reason why EPA is taking the stance of strict regulation of arsenicals.[1711, 1716]

There are channels by which unused and unopened containers of the arsenites can be returned to the manufacturer for resale. Representatives of the manufacturers also indicated that they would accept contaminated or otherwise unwanted material for reprocessing provided that the reprocessing was possible and that a market existed. Foreign markets for arsenite insecticides exist where the benefits of use outweighs the possible detrimental effects. The export of arsenicals should be licensed only when it can be shown that the materials can be used to create an overall environmentally desirable result. Arsenical pesticides are currently being exported in relatively small amounts (at least 300,000 lbs in 1970).[1738]

5. EVALUATION OF WASTE MANAGEMENT TECHNIQUES

There are six waste management methods which have applicability to the arsenite compounds and which are currently being used or which might be applied at a National Disposal Site. These methods apply mainly to the arsenite compounds used as insecticides. The herbicides and soil sterilizers are not expected to create a disposal problem in that if they ever require disposal they can be applied under new highway pavement and similar construction which requires sterile soil. It should also be stressed that regardless of the type of waste process employed, it still would be necessary to deal with toxic arsenic in some form. The following is a discussion of the options for the management of arsenite insecticides.
insecticides.

Option No. 1 - Recycle/Reuse

Representatives of the three remaining manufacturers of arsenic pesticides have stipulated the conditions under which these materials were returned to them for reprocessing or resale in the past. Each firm accepted these arsenite materials for resale without any reprocessing if the batch had originally been made by the firm and if the materials were in their original unopened containers. Each firm above expressed its reluctance to accept the product of other firms. Given the hypotehtical situation of a batch of materials which was unusable but was refinable, each firm indicated its willingness to accept it for reprocessing provided that there was an available market for the material.[1555, 1711, 1712]

Option No. 2 - Long Term Storage

The use of large, weatherproof and siftproof storage bins or silos is currently being used for the storage of other arsenic compounds, especially arsenic trioxide.[1547] Unwanted arsenites, already packed in the manufacturer's containers, could also be stored in these large weatherproof bins. This approach is a relatively expensive one which requires land and storage equipment in need for long, unknown periods of time before these materials can be moved by sale or disposal to other outlets. Insofar as the arsenic compounds are poisonous in any form, long term storage is a safe method for managing the arsenite wastes.

Option No. 3 - Land Spreading

Some users, when faced with unwanted stocks of some arsenite materials, use land spreading as a means of disposal. This approach involves spreading the waste materials over large amounts of land in very light applications so as not to significantly affect any of the crops or plant life growing in in the vicinity. This technique might be used for rare or infrequent disposal of small amounts of waste but in light of the fact that these compounds will build up in the soil by repeated application, this method cannot be considered as completely adequate and other methods should be considered first.

Option No. 4 - Export

Export of arsenite compounds, discussed previously, is not a disposal process but is a means of arsenical management preventing large unwanted overstocks provided that the advantages of their foreign use outweigh any detrimental effects. It should not be considered for the sole purpose of solving a U.S. problem at the expense of a foreign country.

Option No. 5 - Process for Recovery of Metals in Arsenic Trioxide

American Smelting and Refining (ASARCO) has a process operating at its Tacoma, Washington plant whereby they are recovering lead, copper, zinc and possible other metals from smelter dust which contain large amounts of arsenic trioxide. The details of the process are proprietary to ASARCO but it is conceivable that this basic process might be employed to recover lead, zinc and copper from the arsenical insecticides and herbicides as well. But it should be remembered that this process would still result in the production of arsenic trioxide which is a disposal problem in its own right.[1547]

Option No. 6 - Landfill

Disposing arsenite compounds in typical landfills is not recommended because of their high toxicity and slight solubility. However, should the stocks of any arsenic compounds become unmanageably large (especially As_2O_3), the use of expensive encapsulation or safer sites such as abandoned quarries or mines may be required. Other options should in any case be considered first.

Summary of Available Waste Management Techniques

The available waste management techniques are as follows:

Option	Remarks
Long term storage	Best method if stocks are small or future use is projected
Export	Good only if appropriate use is assured
Stable Landfill	May replace long term storage if stocks become large
Recycle/Reuse	Returned stocks currently resold by manufacturers
Metals/As_2O_3 Recovery	Process not recommended for disposal site
Land Spreading	Generally unsatisfactory

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Processes for treating arsenite wastes should not be included in a National Disposal Site scheme but the site still should be chartered to accept all forms of arsenic containing materials that are transported to it. Once at the site, it is believed that the best approach is long term storage prior to shipment from the National Disposal Site for some useful purpose. The market outlook for inorganic arsenic pesticides is weak since additional EPA restrictions on arsenic compounds are expected. It is believed that sodium arsenite, in particular, will still have use as a soil sterilant. Therefore the amounts of transportable waste inorganic arsenite compounds projected for the next five years are very small and do not in themselves justify the need for treating arsenic compounds other than storing them until they can be disposed of by export or use. Return of acceptable stocks to manufacturers for immediate resale is also recommended but reprocessing before resale is not expected to be performed on any significant scale. The following waste management techniques for national disposal sites are listed in order of preference.

	Option	Remarks
Best:	Long Term Storage	Best current method for handling arsenite wastes
	Landfill	Site must be safe
	Metals and As_2O_3 Recovery	Process not recommended for disposal site
	Recycle and Reuse	Least feasible 1) Already performed by manufacturer 2) Non-applicable if arsenites are banned

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Copper Acetoarsenite

IUC Name

Common Names

Structural Formula

$(CH_3COO)_2 Cu \cdot 3 Cu(AsO_2)_3$ *

Molecular Wt.[1] 669(3)* Melting Pt.[2] Boiling Pt.

Density (Condensed) @ ° Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water slightly soluble(3) Hot Water Ethanol

Others: soluble in dil. acids

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in fiber drums, metal pails and cans

ICC Classification poison class B Coast Guard Classification poison class B

Comments

Oral LD_{50} in rats = 22 mg/kg(2) insecticide, wood preservative, pigment for ships(2) *Not officially accepted.

References (1) 0766
(2) 1492
(3) 1742

[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium arsenite

IUC Name Potassium meta arsenite(1)

Common Names

Structural Formula

$KAsO_2$(1)

Molecular Wt.[1] 146.02(1) Melting Pt.[2] Boiling Pt.

Density (Condensed) @ ° Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water sol.(1) Hot Water sol.(1) Ethanol slightly sol.

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison Class B Coast Guard Classification

Comments Very poisonous. LD_{50} for rates orally is 14 mg/Kg. Mieron manufacture - reduce silver salt to metallic silver(2). 1) Merck says item of commerce is approx. $KAsO_2$-$HAsO_2$(2). 2) Made into Karsenite solution, Fowlers solution for medicine for chronic dermatides, charea(2)

References (1) 1570
(2) 1492
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium arsenite

IUC Name Potassium ortho arsenite

Common Names

Structural Formula

K_3AsO_3 (1)

Molecular Wt.[1] 240.23(1)

Melting Pt.[2]

Boiling Pt.

Density (Condensed) @ °

Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point °

Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water very sol.(1) Hot Water Ethanol sol.(1)

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison class B

Coast Guard Classification

Comments Very poisonous. LD_{50} for rates orally is 14 mg/Kg. Mirror manufacture - reduce silver salt to metallic silver(2). 1) Merck says item of commerce is approx. $KAsO_2$-$HAsO_2$(2) 2) Made into K arsenite solution (Fowlers solution) for medicine for chronic dermatitus, chorea(2)

References (1) 1570

(2)

(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc arsenite

IUC Name Zinc in-Arsenite

Common Names

Structural Formula

$Zn(AsO_2)_2$(1)

Molecular Wt.[1] 279.2(1) Melting Pt.[2] Boiling Pt.

Density (Condensed) @ ° Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Low solubility(2) Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B Coast Guard Classification Poison B

Comments Highly toxic, a wood preservative, insecticide. Toxicity similar to calcium arsenate(2)

References (1) 0766

(2) 1742

(3)

[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead arsenite

IUC Name Lead ortho arsenite(1)

Common Names

Structural Formula

$Pb_3(AsO_3)_2 \cdot XH_2O$

Molecular Wt.[1] 954.45 $+XH_2O$ Melting Pt.[2] Boiling Pt.

Density (Condensed) 5.85(1) @ ° Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insol.(1) Hot Water Ethanol

Others: S Alk and NHO_3

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison class B Coast Guard Classification Poison class B

Comments Emits toxic fumes on heating(2) insecticide is only listed USE)3

References (1) 1570

(2) 0766

(3) 1492

[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead arsenite

IUC Name Lead meta arsenite

Common Names

Structural Formula

$Pb(AsO_2)_2$ (1)

Molecular Wt.[1] 421.03(1)

Melting Pt.[2]

Boiling Pt.

Density (Condensed) 5.85 g/cc @ °

Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point °

Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insol.

Hot Water

Ethanol

Others: sol. acids

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison Class B

Coast Guard Classification Poison Class B

Comments Emits toxic fumes on heating(2). Insecticide only listed use(2)

References (1) 1570
(2) 0766
(3) 1492

[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Calcium arsenite

IUC Name

Common Names Mono calcium arsenite(3)

Structural Formula

$CaHAsO_3$(2)

Molecular Wt.[1] 164.00(1)

Melting Pt.[2]

Boiling Pt.

Density (Condensed) @ °

Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ °

@ °

@ °

Flash Point °

Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water

Hot Water

Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison class B

Coast Guard Classification Poison class B

Comments used as insecticide and germicide; no other listed uses(2). White powder of varying composition. High mammalian toxicity(3)

References (1) 1570
(2) 0766
(3) 1492

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium arsenite

IUC Name Sodium meta arsenite

Common Names

Structural Formula

$NaAsO_2$(1)

Molecular Wt.[1] 129.91(1)   Melting Pt.[2]   Boiling Pt.

Density (Condensed) 1.87 g/cc @ °   Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ °   @ °   @ °

Flash Point °   Autoignition Temp. °

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water very sol.(1)   Hot Water very sol.(1)   Ethanol slightly sol.

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in steel drums, 55 gallon max(2)

ICC Classification poison class B(2)   Coast Guard Classification poison class B(2)

Comments used in manf. of arsenical soaps, termites, and herbicides for RR and highway weed control(3)

References (1) 1570
(2) 0766
(3) 1492

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[1] Give a reference for each entry.

[2] Supply units where necessary

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PROFILE REPORT

Chloropicrin (111)

1. GENERAL

Chloropicrin is a slightly oily, colorless liquid boiling at 112 C and solidifying at -69 C. It is a powerful irritant and affects all body surfaces. It causes lachrymation, vomiting, bronchitis, and pulmonary edema.[766]

This material is primarily used as an insecticide and parasiticide[1492] for disinfecting cereals and grains. It is called vomiting gas and has been extensively used by the military as a war gas.[0766]

Chloropicrin is made by the chlorination of nitromethane in the presence of calcium carbonate, or by the reaction of picric acid with sodium hypochlorite.[1316] It is also produced commercially by reacting sodium hypochlorite with nitromethane.[1749]

Commercial facilities for the manufacture of chloropicrin are operated by Dow Chemical Company[1718], International Minerals & Chemical Corporation[1718], Niklor Chemical Co., Inc.[1749] and Sobin Chemical Incorporated.[1750]

2. TOXICOLOGY[766]

Chloropicrin is a powerful irritant and affects all body surfaces. It causes lachrymation, vomiting, bronchitis, and pulmonary edema. A concentration of 1 ppm causes a smarting pain in the eyes and therefore, in itself constitutes a good warning of exposure. It causes vomiting, probably due to swallowing saliva in which small amounts of chloropicrin have dissolved. Its primary lethal effect is to produce lung injury and it is a difficult gas to protect oneself against because it is chemically inert and does not react with the usual chemicals used in gas masks.

3. HEALTH AND SAFETY

Four parts per million chloropicrin in air is sufficient to render a man unfit for action and 20 ppm, when breathed from one to two minutes, causes definite bronchial or pulmonary lesions. Chloropicrin emits highly toxic fumes when heated to decomposition.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation and Personnel Safety in Dealing with Concentrated Allyl Chloride

Gloves and chemical goggles should be worn to protect the skin and eyes when handling chloropicrin. If it is necessary to be in discomforting concentrations of chloropicrin vapor, a fullface gas mask with a canister recommended for use in acid gases and organic vapors should be worn.

Chloropicrin is shipped as pure material and as mixtures with nonflammable, nonliquified compressed gas, and mixtures containing no compressed gas. Regulations covering the shipping of these materials are found in Federal Code of Regulations.[0278] Glass and steel containers are suitable for shipping chloropicrin. Containers and handling equipment made of aluminum, magnesium or their alloys should not be used in chloropicrin service as under certain conditions these materials are severely corroded.

Chloropicrin should be stored in tightly closed containers in a cool place away from any dwellings. In outside storage, drums should be stored on their sides to prevent water from collecting around the bungs.

Disposal/Reuse of Waste Chloropicrin Streams

A definition of acceptable criteria for the disposal of chloropicrin must also take into account acceptable criteria for the release of hydrogen chloride, hydrochloric acid and nitrogen oxides to the environment, since current practice in chloropicrin disposal involves some processes that reduce chloropicrin to these materials.

Current techniques utilize incineration, land burial and lagooning. The recommended maximum concentrations of chloropicrin, hydrogen chloride, hydrochloric acid, and nitrogen oxides in effluent streams released to the environment are as follows:

Contaminant and Environment	Maximum Concentration and Point Source Release Rate	Basis of Recommendation
Chloropicrin released to the atmosphere	0.001 ppm (0.007 mg/M^3)/24 hr.	0.01 TLV
Hydrogen chloride released to the atmosphere	0.05 ppm (0.07 mg/M^3)/24 hr.	0.01 TLV
Hydrochloric acid released to the atmosphere	0.05 ppm (0.02 mg/M^3)/24 hr.	0.01 TLV
Nitrogen oxides released to the atmosphere	0.05 ppm (0.07 mg/M^3)/24 hr.	0.01 TLV

5. EVALUATION OF CURRENT AND NEAR FUTURE CHLOROPICRIN DISPOSAL PROCESSES

Chloropicrin is expected to appear primarily as dilute aqueous and organic waste streams and only rarely as concentrated waste. The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Concentrated Chloropicrin

In the event it became necessary to dispose of a significant quantity of concentrated chloropicrin, two disposal options are available. The first option is to contact the manufacturer and determine if it is possible to return the materials. Niklor Chemical Company,[1749] and Sobin Chemical Incorporated,[1750] have indicated that recycling of chloropicrin is possible, depending on the contaminating material. The second option is incineration but since chloropicrin is non-flammable, it must be added to fuel or sprayed into an incinerator at high temperatures. Scrubbers must be used to remove unwanted contaminants from the effluent gas stream (Table I). Both options provide adequate ways to handle the concentrated waste but it is strongly recommended that recycling be used whenever possible.

Dilute Aqueous Waste

Dilute aqueous waste containing chloropicrin is lagooned and allowed to gas off,[1750] or is incinerated with scrubbers to remove the hydrogen chloride from the effluent gas.[1772] It is recommended that the material to be lagooned be reacted with sodium sulfite or sodium bisulfite to suppress the noxious properties of the chloropicrin and any resulting sludge be incinerated or buried in an approved landfill. Both lagooning and incinceration are adequate means of disposing of chloropicrin provided the recommended concentrations released to the environment are not exceeded (Table I).

Dilute Organic Waste

Dilute organic waste generated during the manufacture of chloropicrin are disposed of either by land burial,[1750] or incineration.[1772] Incineration with proper scrubbing of the effluent gas to remove hydrogen chloride and nitrogen oxides is the primary option for disposing of dilute organic waste. An alternate method of disposal would be in an approved chemical landfill.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Chloropicrin is expected to appear primarily as dilute organic and aqueous wastes, and to a much lesser degree as concentrated waste. Facilities for handling the disposal of these wastes are located at the manufacturing sites and are adequate if the chloropicrin is disposed of by the means discussed in Section 5. This material is not judged to be a candidate for National Disposal Sites.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET #111

H. M. Name Chloropicrine

IUC Name Nitrotrichloromethane[1]

Common Names Chloropicrin[1], Nitrochloroform[1]
Trichloronitromethane

Structural Formula

Cl_3CNO_2[1]

Molecular Wt.[1] 164.38 Melting Pt.[1] -64 C Boiling Pt.[1] 112^{757} C

Density (Condensed) 1.6558 @ 2014 C Density (gas) 5.69[4] @

Vapor Pressure[2] (recommended 55 C and 20 C)

18.3 mm @ 25 C 40 @ 33.8 C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.16% @ 20 C[2] Hot Water Ethanol Soluble[1]

Others: Soluble in acetone[1], benzene[1], methanol[1], Acetic acid[1], ether[3]

Acid, Base Properties May be corrosive under certain conditions.

Highly Reactive with

Compatible with Fuel oil, kerosene

Shipped in Glass, steel containers and in steel containers as nonliquified compressed gas[6]

ICC Classification Poison A[4] Coast Guard Classification Poison B[4]

Comments Non-flammable[5]

References (1) 1570 (4) 766
(2) 1618 (5) 509
(3) 1492 (6) 278

Give a reference for each entry.

Supply units where necessary

PROFILE REPORT

Chrome (113)

1. GENERAL

Introduction

Chromium is a metallic element with properties resembling iron, and which occurs mainly in chrome/iron ore ($FeO \cdot Cr_2O_3$). It is a very infusible, hard, gray metal which is incorporated in the manufacture of stainless steel and other corrosion resistant alloys. Chrome is extensively used as a plating on other metal surfaces to give a hard, corrosive resistant, beautiful surface and also finds wide use as a catalyst.[1570]

The ferro chromium alloys are made by silicon reduction of chromite ores in a two-stage process. Initially a high silicone ferro chromium is produced in a submerged arc furnace. Then this product is treated in an open arc type furnace with a synthetic slag containing Cr_2O_3.[1433] To produce chromium metal either electrolytically or by the reduction of chromium compounds, a chemical treatment is necessary to remove the iron and other impurities from the starting materials. Reduction methods start with chromium oxide Cr_2O_3 which has been obtained from chromite ore via sodium bichromate. Commercial chromium metal is produced by reducing Cr_2O_3 with aluminum, although silicon and carbon are sometimes also used as reducing materials. The aluminum reaction is performed in a refractory lined vessel which contains the exothermic, self-sustaining reaction. Chromium metal can also be produced by the electrowinning of chromium from either chrome alum or chromic acid electrolytes.[1433] As far as can be determined by a review of the literature, no significant amounts of chromium metal appear as wastes from the production processes.

In 1968 approximately 300,000 short tons of chromium were consumed in chromium ferro allloys and chromium metal in the United States. The greatest proportion was used in various ferro chromium alloys. This represents 60 to 70 percent of the chromium ore processed in the U.S.[1975]

Occurrence as a Waste Product

Chromium, either as a ferro alloy, stainless steel, metallic catalyst or plate, is relatively valuable and normally is not disposed of without reuse. Stainless steel and other alloys have considerable value as scrap metal and these are normally recycled. Chromium plate on scrap metal, such as that coming from scrapped automobiles, normally is recycled, not necessarily for the chrome plate but for the scrap steel. The chrome is believed to be melted down without any prior removal of the chrome plate. The occurrence of ferro chrome alloys and chrome plated metal as recycled scrap is widespread in the United States. In the scope of this study, it is not possible to determine the degree by which chrome metal is actually being lost in junk yards and trash dumps without any attempt at recovery.

2. TOXICOLOGY

Zero valent chromium, as the pure metal or alloy, is considered to be essentially non toxic to plants and animals.[1492]

3. OTHER HAZARDS

The dust of chromium metal is considered a moderate fire hazard.[0766] Chromium metal does not exhibit any other hazards.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Chromium does not require special handling when it occurs as a waste in alloys or as a decorative plate on other metal surfaces. The industries that use large amounts of chrome and chrome alloy materials should have a program by which the various types of chrome containing scrap materials are collected and segregated for recycling. No safety precautions are required for the handling of the scrap materials except those which would normally be used for the handling of other common scrap metals.

5. EVALUATION OF WASTE MANAGEMENT OPTIONS

There is only one feasible waste management option for chrome metal and chrome metal alloys which is that of recycling scrap for use in new products. There is a considerable market for this type of scrap material and it is believed that all major industries who work with these metals have a program by which the scrap is segregated and saved for sale to a scrap dealer.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Waste chromium metal and chrome alloys are not candidate materials for National Disposal. They are essentially non-toxic to both plant and animal life. Additionally, they are very corrosion resistant and do not weather to produce harmful corrosion products. Waste chrome metals and their alloys have inherent value and scrap recovery and recycle programs are widespread in the industry.[1975]

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chrome

IUC Name

Common Names

Structural Formula

Cr(1)

Molecular Wt.[1] 51.996(1)   Melting Pt.[2] 1890C(1)   Boiling Pt. 2482(1)

Density (Condensed) 7.20(1) @ 28 C(1)   Density (gas) N/A @ °

Vapor Pressure (recommended 55 C and 20 C)

@ °   @ °   1 mm @ 1616C(2)

Flash Point N/A °   Autoignition Temp. °

Flammability Limits in Air (wt %)   Lower N/A   Upper N/A

Explosive Limits in Air (wt. %)   Lower N/A   Upper N/A

Solubility

Cold Water insoluble(1)   Hot Water insoluble(1)   Ethanol

Others: sol in dil H_2SO_4, HCl

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments Moderate fire hazard in dust form(2)

References (1) 1570
(2) 0766
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

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PROFILE REPORT
Chromic Acid (114)

1. GENERAL

Introduction

Chromic acid is the common name given to chromium VI trioxide, CrO_3. It is also known as chromic anhydride. It is a poisonous, powerfully oxidizing, red, solid material. It is used almost exclusively in the metal finishing industry where approximately half is used in direct decorative chrome plating and the remainder is used in an assortment of metal treating baths including etching, passivation, and conversion coating.[1981] The annual consumption for chromic acid is estimated to be approximately30,000 tons with 90 percent being used in the metal treating industry and the remaining 10 percent used for catalyst manufacture, refractory, or exported.[1506]

Manufacture of Chromic Acid

Chromic acid is produced by the reaction of sodium dichromate and sulfuric acid. Oleum, i.e. sulfuric acid charged with sulfur dioxide, is also commonly used.[1982, 1983] The mixture is heated to about 400 F whereupon the mixture separates into a chromic acid layer and an upper, less dense, sodium bisulfate layer. The layer containing the product is drawn off and solidified on water cooled flaking rolls while the bisulfate layer, which contains small amounts of chromium compounds, is returned to the supplier for reuse in making sodium dichromate.[1433, 1983] Normally there is no refining of any large amounts of this product which is characteristically 99.5 percent pure. The product is either sold as flake or is ground before packing in steel drums. There is no significant liquid effluent from the process except for occasional water washes from cleaning the process equipment. These washings are directed to sumps or evaporation ponds on the factory premises.

Sources of Waste Chromic Acid

The metal finishing and chrome plating industry is responsible for very large amounts of chromic acid wastes. It is estimated that between 25,000 and 30,000 tons of chromic acid will be consumed in the metal finishing industry in 1972.[1506] Losses occur from metal treating tanks which are customarily dumped as they load up with grease, dirt, etc. The other major source of wasted chromic acid arises from dragout, i.e. the losses that occur from rinsing the parts after plating and metal treating. Equipment is available to minimize losses from dragout and recover reusable water, but the expense in purchasing this equipment cannot normally be justified in terms of the value of recoverable chromic acid. The waste management problems of chromic acid, as well as other hexavalent chrome compounds, are detailed in the Profile Report which discusses the ammonium, potassium, and sodium salts of the chromates and dichromates.

2. TOXICOLOGY

Chromium trioxide CrO_3, when dry or in solution as chromic acid, is a very corrosive material and a strong oxidizing agent. If it contacts skin or mucous membranes, it can produce ulcerous lesions which heal slowly. The salts of chromic acid have also been associated with lung cancer. The Threshold Limit Value (TLV) for hexavalent chromates (Cr VI) is 0.1 mg/m^3 in air.[0225] Drinking water should contain no more than 0.05 ppm.[1752] The corrosive nature of chromic acid dictates that the material should also be kept away from contacting terresterial plant surfaces. No exact information was available regarding the harmful effects of chromic acid on aquatic plant and animal life but it is reasonable to assume that chromic acid is potentially very harmful.

3. OTHER HAZARDS

Chromic acid does not present a critical flammability or explosive hazard by itself, but since it is a powerful oxidizing agent, it should not be mixed with organic materials or other reducing agents. Even dilute organic solutions containing chromic acid should not be heated for fear of a violent reaction.[0215] Chromic acid is not corrosive to metals in the anhydrous state but concentrated aqueous solutions will attack some metals the least resistant of which are copper and its alloys (brass).

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transporation

When occurring as a concentrated waste product either in solid or solution form, chromic acid must be stored away from high temperatures or reducing agents. The correct container must be used for the solid or solutions. The creation of CrO_3 dust must be avoided during storage, transfer and handling of the material. Workers should be adequately protected from contact of chromium trioxide with skin, eyes, or internal organs. Since small ingested amounts can cause permanent injuries or death, adequate supervisory control of all operations and education of employees on the hazards of chromium trioxide is recommended.

General information on the properties and safe handling guidelines of chromium trioxide are found in the data sheet of the Manufacturing Chemists Association.[0215] Any and all additional Federal regulations governing the handling, storing, loading, and shipping of these materials are to be obeyed.

Disposal/Reuse

The Federal Water Quality Act of 1965 limits the discharge, to open waterways, of chromium trioxide and all other hexavalent chrome compounds. Each state is allowed to set its own upper limit for hexavalent chromium discharge but it is felt that the limits will all be set near 0.05 ppm which the U. S. Public Health Service has set for drinking water standards.[1752] The upper limits of hexavalent chromium discharge to municipal sewage systems is normally set by local authorities at about 0.05 ppm, a relatively low concentration, since this material, when more concentrated, can cause severe problems with biological water treatment processes in sewage treatment plants. Practically speaking, this maximum discharge limit is very often ignored when the discharge point is far enough from the water treatment plant so that adequate dilution is usually achieved. Additionally it is felt that hexavalent chrome is almost always reduced to Cr III and precipitated as the sulfide while in transit within the sewer by various other chemicals contained in the sewage.

The metal finishing industry has been placed under pressure to control the amount of chromium trioxide that is being wasted to sewers and landfills but in many areas the water quality officials have not set levels of compliance or they are still allowing large discharges.[1473] Technology is rapidly developing which will enable the industry to economically recover a significant part of chromic acid for reuse, but the current general concensus is that while the technology may exist, the costs are still too high for economical operation in the average size metal finishing facility. The economics of chrome products may force the installation of chrome recovery. The types of processes which already have applicability towards chromic acid recovery include ion exchange and possibly reverse oxmosis. Systems under consideration for potential applicability include electrodyalysis and liquid extraction.

5. EVALUATION OF CURRENT OR NEAR FUTURE WASTE MANAGEMENT TECHNIQUES

Equipment and processes to handle waste chromic acid in solution can be divided into two main groups. The first group covers the equipment and methods to conserve chromium compounds by reconcentrating, purifying, and reusing them, or returning the concentrates to the manufacturer for reprocessing. The other group covers the method of treating hexavalent chrome for ultimate disposal such as sewering or landfill without any attempt at recovery or reuse. The waste treatment processes and equipment are identified (Table I), and discussed in considerable detail in the Profile Report on the ammonium, potassium, and sodium salts of chromate and dichromate anions:

6. APPLICABILITY TOWARDS NATIONAL DISPOSAL SITES

A batch process facility for chemical reduction and precipitation should be included in the National Disposal Sites for management of concentrated chromic acid wastes which are accepted for ultimate incineration or landfill. The reduction to Cr^{III} is preferred over direct precipitation of Cr^{VI} because the required lead and barium reagents are highly poisonous, expensive and require large excesses to precipitate below safe levels. The only reason for direct precipitation would be for pigments which is not normally economical. Precipitation of these materials, while not conserving chromium resources, is currently the most reasonable approach for handling these substances based upon current chrome prices (Table I). The sub-process of electro reduction could have merit in replacing the usual chemical reduction step. This very same batch process facility would be usable for many of the other heavy metal compounds which could also occasionally require disposal. These include cadmium, mercury, lead, copper, nickel, antimony and arsenic.

The permanent containment and storage or proper landfilling of the resultant chromium waste sludges or their incinerator residues are recommended. The economics for transportation to the landfill or storage site will have to be considered someday in the decision to transport the hydrated sludge or to incinerate it prior to shipment. In addition, incinerating or dewatering the sludges should also be considered in an effort to make the entire disposal process more efficient from the standpoint of metals recovery.

The other processes mentioned (ion exchange, ion flotation, dialysis, reverse osmosis, liquid/liquid extraction, etc.) will result in reduced amounts of chromic acid wastes when they are employed in the metal finishing industry, but they are not applicable to National Disposal Sites since they are designed to process dilute aqueous wastes which could not economically be transported to a National Site. However one of these processes might be incorporated to purify the water used within the Disposal Site itself.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Chromic Acid

IUC Name Chromium Trioxide

Common Names Chromic Anhydride

Structural Formula

CrO_3

Molecular Wt.[1] 100.01 Melting Pt.[2] 197C decomposes Boiling Pt. _____

Density (Condensed) 2.70 @ 20 C Density (gas) _____ @ _____ ° _____

Vapor Pressure (recommended 55 C and 20 C)

_____ @ _____ ° _____ @ _____ ° _____ @ _____ °

Flash Point noncombustible ° Autoignition Temp. _____ °

Flammability Limits in Air (wt %) Lower N/A Upper N/A

Explosive Limits in Air (wt. %) Lower N/A Upper N/A

Solubility

Cold Water 164.9g/100g at 0 C Hot Water 206.7g/100g at 100C Ethanol _____

Others: H_2SO_4

Acid, Base Properties concentrated solutions at elevated temperatures attack most common metals and some plastics

Highly Reactive with readily oxidisable organics(may ignite); intimate contact with powerful reducing agents can cause violent explosions(2)

Compatible with certain oxidant-resistant plastics and mild steel

Shipped in steel barrels or drums, ICC spec. 6A, B or C or 17H, 37D, 37E

ICC Classification oxidizing material* Coast Guard Classification oxidizing material

Comments TLV(ACGIH) 0.1 mg/m^3 air

*in solution DOT classification is corrosive liquid, white label, 1 gallon max.

References (1) 0215

(2) 0766

(3) _____

[1] Give a reference for each entry.

[2] Supply units where necessary

TABLE 1

METHODS OF CHROMIUM TRIOXIDE CONCENTRATION FOR WATER PURIFICATION AND MATERIAL REUSE

Method	Remarks
Ion Exchange	Used in last 10 to 15 years for industrial chromate removal.
Ion flotation	Not developed enough for industrial use.
Electrodialysis	Not yet efficient enough for industrial use.
Adsorption on activated carbon	Efficient for final water polishing but creates problem of used carbon disposal.
Liquid-liquid extraction	Shows high merit but is only in early development stages
Reverse osmosis	Installations exist but not for chromates. Technology developing rapidly.

METHODS FOR UNRECOVERABLE FINAL DISPOSAL

Reduction to Cr III and precipitation by pH adjustment	Use is widespread in industry. Precipitates are normally landfilled.
Direct precipitation with barium or lead	Efficient method if market available for the precipitates as pigments. Not frequently used.
Electrochemical conversion to Cr III	Can be used to reduce to Cr III prior to precipitation, thereby eliminating need for reducing chemicals. Shows promise.

PROFILE REPORT ON 2,4-D (135)

1. GENERAL

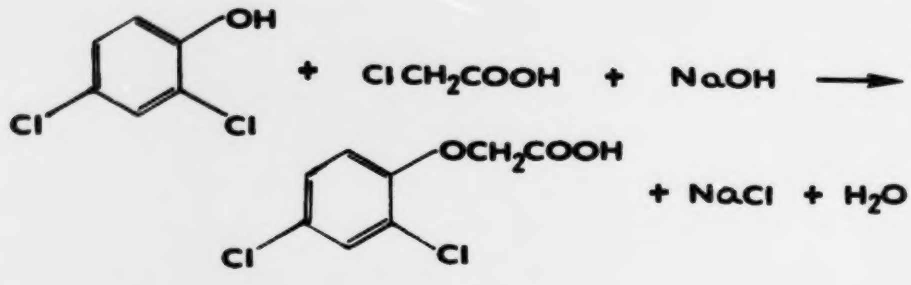
Introduction

The discovery of the growth regulating properties of the chlorinated phenoxyacetic acids in 1944 and their subsequent employment as herbicides began the modern era of selective chemical weed control. These compounds are selective to broad-leaved weeds in cereals and could be absorbed from soil as pre-emergent herbicides. The growth regulating action is shared by a group of hundreds of related molecules all derived from the same parent substance, 2,4-dichlorophenoxyacetic acid or 2,4-D. In fact, to permit the proper application and formulation of 2,4-D, the amine salts and esters of the acid have been generally used instead of 2,4-D as such.

The chlorophenoxy groups of herbicides which includes 2,4-D, 2,4,5-T (2,4,5-trichlorophenoxy acetic acid) and MCPA (2-methyl-4-chlorophenoxy acetic acid) comprise approximately half the total domestic herbicide market. The U.S. production figures for 2,4-D from the year 1960 to 1967 in thousands of pounds are[449,1610]: 1960, 361,815; 1961, 43,392; 1962, 42,997; 1963, 46,312; 1964, 53,714; 1965, 63,320; 1966, 68,182; 167, 77,139. However, in 1970 only 43,576,000 lb. of 2,4-D were produced.[1718] The production figures thus illustrate the gradual declining importance of 2,4-D as a base material for herbicides.

Manufacture

2,4-D is generally prepared by the condensation reaction of monochloroacetic acid and 2,4-dichlorophenol in an alkaline solution at atmospheric pressure, 60 to 80 C, and a residence time of 6 to 8 hr in a jacketed stirred reactor[1610]:



Large scale commercial facilities for the manufacture of technical grade 2,4-D in the United States include the following[1774, 1775, 1776, 1777, 1778, 1779, 1780]:

Dow Chemical Company, Midland, Michigan
Rhodia Inc., Chipman Division, Portland, Oregon
Transvaal Inc., Jacksonville, Arkansas

The Transvaal plant was formerly operated by Hercules Inc.

Uses

The chlorophenoxy acids are active by contact and by translocation from leaves to roots of perennial weeds and are used as pre-emergent applications to the soil for control of young seedlings. They are also effective for aquatic weed control, for the elimination of unwanted vegetation, and are selective against many broad-leaved annual weeds in cereal and grass crops.[509]

In addition, 2,4-D and its derivatives have also found important uses in related fields such as thinning of fruit, prevention of preharvest drop, fruit setting, promotion of rooting and postharvest decay prevention.[509]

Sources and Types of Pesticide Wastes

The sources of pesticide wastes may include the following[620]: (1) pesticide manufacturers; (2) pesticide formulators; (3) pesticide wholesalers; (4) professional applicators; (5) cooperage facilities that recondition drum; (6) agricultural users; (7) government facilities that store, transport, and use pesticides; (8) urban and suburban home and garden users; (9) commercial and industrial processes including those from rug and fabric treatment facilities manufacturing plants, hospitals, etc.

In general, pesticide wastes can be classified as either diluted or concentrated wastes. Diluted pesticide wastes include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent caustic solutions used to clean empty pesticide containers. Concentrated pesticide wastes include any unused or contaminated pesticides, pesticide materials left in containers after emptying, sludges formed in treating waste water containing pesticides, sawdust or straw used to soak up accidental pesticide spills.

Unlike most pesticides, 2,4-D is also used as an aquatic herbicide and applied directly to lakes, rivers, irrigation waterways, and other surface waters for weed control, thus posing a potential water pollution problem. 2,4-D has been reported to persist for several months in lake waters.[1757]

Physical and Chemical Properties

The physical and chemical properties of 2,4-D are summarized in the attached worksheet.

2. TOXICOLOGY

2,4-D is of moderate acute toxicity to mammals. The acute oral and dermal LD_{50} values to the rat have been reported to be 375 and 1500 mg/kg body weight respectively.[1277] Inhalation of 2,4-D dusts and sprays is relatively harmless, and percutaneous absorption is negligible.[449]

Chronically 2,4-D is of low toxicity, and can be ingested by animals and man in daily dosages approaching those which produce acute toxic effects when given only once. Thus, the cumulative effects of 2,4-D are minimal.

The American Conference of Governmental Industrial Hygienists 1971 recommended Threshold Limit Value (TLV) for 2,4-D in air is 10 mg/M^3.[225]

The 48-hour Median Tolerance Limit (TL_m) for 2,4-D established by the Federal Water Pollution Control Administration for various types of fresh water organisms in micrograms per liter are[536]: P. Californica (stream invertebrate), 1,800; Daphnia pulex (cladocerans), 3,200; Rainbow trout (fish), 960; and Gammarus lacustris, 1,800. These data are indicative of the hazards to aquatic life associated with the use of 2,4-D.

3. OTHER HAZARDS

As an organic acid, 2,4-D is corrosive and reacts with metals and bases. When heated to decomposition, highly toxic fumes of hydrogen chloride and other chlorinated products are emitted.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Although 2,4-D is only mildly toxic to humans, the use of rubber gloves, goggles, and a respirator is recommended in its handling and application. Storage of 2,4-D should be in a cool, dry, well-ventilated area, away from acute fire hazards, and with proper warning signs posted. No Department of Transportation shipping labels are required for 2,4-D, as the hazards in shipping 2,4-D are generally considered as minimum.[278]

The National Agricultural Chemicals Association has established a Pesticide Safety Team Network with Area Coordinators throughout the country to provide nationwide 24-hour service. The network became operational on March 9, 1970 (with a central telephone number - [513] 916-4300) and should be consulted in all cases of accidents, spills, leakage, fires, and other types of disasters involving 2,4-D.

Disposal/Reuse

Contaminated or degraded 2,4-D could not be practically considered for reprocessing. The safe disposal of 2,4-D is defined in terms of the recommended maximum concentrations released to the atmosphere and a potable water source and/or marine habitat. These recommended maximum concentrations are as follows:

Contaminant in Air	Maximum Concentration for Continous Exposure	Basis for Recommendation
2,4-D	0.1 mg/M^3/24 hours	0.01 TLV

Contaminant in Water	Maximum Allowable Concentration	Basis for Recommendation
2,4-D	10 μg/liter	0.01 48-hour TL_m for fish life

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Dilute Pesticide Wastes

Option #1 - Adsorption with Powdered Activated Carbon. The effectiveness of powdered activated carbon on the removal of 2,4-D from water has been examined by Aly and Faust,[1789] Sigworth,[1635] and Whitehouse.[445] Aly and Faust constructed adsorption isotherms for 2,4-D in accordance with the Freundlich equation, from which the amount of activated carbon required to reduce the 2,4-D concentration in water from 10 ppm to 1 ppm and 0.1 ppm was calculated to be 85 mg/liter and 318 mg/liter respectively. Sigworth's studies were conducted with initial 2,4-D concentrations of 1 and 6 ppm; however, the results obtained were inconclusive because of the possibility of employing inaccurate analytical procedures. Whitehouse investigated the effects of pH, contact time, and carbon dosage on 2,4-D removal from water, and showed that with an initial 2,4-D concentration of 100 ppm over 90 percent removal of 2,4-D could be achieved at pH values lower than 3.2 after one hour of mixing and a carbon dosage of 300 mg/liter. With a lower 2,4-D initial concentration of 10 ppm, a pH of 6, and one hour contact time, 90 percent 2,4-D removal could be obtained with a carbon dosage of 120 mg/liter and 99 percent 2,4-D removal with a carbon dosage of 320 mg/liter. Based on the results of the studies of Faust and Aly and Whitehouse, the addition of powdered activated carbon to a liquid solution (preferably at a lower pH) followed by stirring and filtration is an adequate method for treating dilute 2,4-D wastes.

Option #2 - Adsorption with Granular Activated-Carbon Beds. Although the effectiveness of granular activated-carbon beds to remove 2,4-D from water has not been discussed in the literature per se, Robeck et al reported that following passage through the carbon columns, the concentration of 2,4,5-T (which is simply 2,4-D with an additional aromated chlorine) in water was reduced from 3.6 ppb to 0.05 ppb.[441] Treatment of waste water containing a variety of pesticide wastes with granular activated-carbon beds have been practiced by Fisons Pest Control Ltd. in England since 1955, where over 99 percent removal of the pesticides are obtained.[1035, 1631] The treated effluent is diluted with river water before discharge to the river, and the results of government biological surveys indicated no effects of the discharge on the river. In the United States, both Rhodia and Dow utilized granular activated-carbon beds in the treatment of their 2,4-D manufacture waste water.[1777,1778] Activated-carbon bed adsorption was also originally employed as the treatment procedure for the waste water from 2,4-D manufacture at the Naugatuck Chemicals plant, Elmira, Ontario, Canada,[1630] although the method was later abandoned due to the high treatment cost associated with the removal of dichlorophenol at that time (1951). Because of the adequate contact time provided and the fact that it is a well established chemical engineering unit operation, adsorption with granular activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute 2,4-D wastes.

Option #3 - Biological Degradation. The biological treatment of 2,4-D waste water has been investigated by Mills[1630] and Sidwell.[1781] Mills reported that 2,4-D acid could be oxidized by bacterial action in the laboratory, but his pilot plant work with trickling filter and activated sludge systems were mainly concerned with the removal of dichlorophenol from the 2,4-D manufacture waste water, and no data on the removal of 2,4-D were given. Sidwell described the Jacksonville, Arkansas project on joint treatment of municipal waste water and 2,4-D manufacture waste water from the Transvaal Inc. plant. Pretreatment of the industrial effluent included processing through a crushed limestone filled neutralization ditch and an in-plant equilization pond, and a final pH adjustment to 7.2 by automatic addition of slaked lime slurry in a continuous stirred pit. The combined municipal-industrial waste water containing 2 to 4.2 mg/liter phenoxy acids was then treated in an aerated lagoon and stabilization pond system before discharge to the receiving stream. Although the removal of chlorophenoxy acids by the lagoon and pond system ranged from only 49 to 80%, the stabilization pond effluent with typically 1.1 mg/liter chlorophenoxy acids was considered to be good quality, as substantiated by the results of the biological surveys of the upper receiving stream conducted in December 1969 and December 1970. The continuous successful operation of the aerated lagoon - stabilization pond system at Jacksonville, Arkansas indicates that 2,4-D containing waste water when combined with sewage could be adequately treated by biological methods.

Option #4 - Ion Exchange. The use of ion exchange columns to remove the sodium salt of 2,4-D from water has been examined by Aly and Faust.[1636] The results of their studies showed that the sodium salt of 2,4-D when present in relatively high concentrations (120 mg/liter) could be completely removed from water by strongly basic anion exchange resins, and indicated that neutralization of 2,4-D to its sodium salt followed by passage through ion-exchange columns is an adequate method for treating dilute 2,4-D wastes.

Option #5 - Removal by Surface Active Agents. The removal of pesticides from water by the use of surface active agents to produce a foam has been investigated by Whitehouse.[445] Although 2,4-D was not included in the study, the results with aldrin and dieldrin showed that up to 90 percent removal was attainable and demonstrated the value of the process as a possible near future treatment method for other types of pesticides.

The other treatment methods for the removal of 2,4-D from water that have been investigated include adsorption with clay, chemical coagulation, and chemical oxidation. The works of Faust and Aly,[446] Schwartz[1756] and Whitehouse[445] all suggested that adsorption with clay was an unsatisfactory method for removing 2,4-D from water. Faust and Aly[446,1636] examined the effects of chemical oxidants on 2,4-D compounds and concluded that both chlorine and potassium permanganate were ineffective in the removal of 2,4-D compounds from water. The laboratory studies of Faust and Aly[446] also showed that chemical coagulation with alum and ferric sulfate doses up to 100 ppm were ineffective in removing 2,4-D. These processes are therefore considered as inadequate methods for treating dilute 2,4-D wastes.

Concentrated Pesticide Wastes

Option #1 - Incineration. The complete and controlled high temperature oxidation of 2,4-D in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of pesticides. The research on incineration of pesticides conducted by Kennedy et al at Mississippi State University has led to the conclusion that 2,4-D approached complete combustion at temperatures as low as 600 C and identified carbon monoxide, carbon dioxide, chlorine and hydrogen chloride as the volatile products from burning of the 2,4-D formulation at 900 C.[62,63] The equilibrium product distributions resulting from the thermal decomposition and combustion of 2,4-D at atmospheric pressure and three temperatures, 1200 C, 800 C, 500 C have also been computed using the TRW Chemical Analysis Program (Table 1). The results also indicate the possible formation of hydrogen chloride, but that at higher air/fuel ratios, complete combustion is approached and both methane and carbon monoxide are only present in small quantities. Incineration is also being considered by Rhodia Inc., Portland, Oregon as a possible means of disposing the solid and semi-solid wastes generated in 2,4-D manufacture.[1777] In addition, combustion units designed for the disposal of chlorinated organic wastes and capable of recovering chlorine in the form of usable hydrogen chloride have been developed, and a 7000 lb/hr plant is now under construction for E. I. du Pont de Nemours & Co. in Victoria, Texas by Union Carbide Corp.[1743] Properly designed and operated incineration is therefore considered as the best present and near future method for the disposal of concentrated 2,4-D wastes.

Option #2 - Chemical Degradation. The use of chemical reagents to decompose concentrated pesticide wastes to less toxic forms has also been investigated by Kennedy et al.[62,63] The Mississippi State work showed that liquid ammonia and metallic sodium or lithium would completely decompose 2,4-D, but the reagents are dangerous to use and the toxicity of the degradation products are not known. The action of caustic alkalies would only hydrolyze 2,4-D to the corresponding salts, and no further degradation could be obtained. Based on these results and the superiority of incineration by comparison, chemical degradation could not be recommended as a method for the disposal of concentrated 2,4-D wastes.

Option #3 - Application to Soil Surface. Research on the reduction of 2,4-D waste process liquors into biologically inactive compounds by means of application to and degradation in the soil surface has been conducted at Alkali Lake in eastern Oregon under the direction of R. L. Goulding of Oregon State University since late 1969.[1754,1755] The results of the study to date suggested subsurface injection of 2,4-D as a useful, economic approach to control airborne losses of the waste component, and indicated clearly the apparent degradation of 2,4-D by soil microorganisms when applied at the rate 250 lb/acre equivalent of 2,4-D. Data derived from samples taken from the actual test plots showed that the 2,4-D concentration in the soil layer subjected to subsurface injection has declined from an initial 135 ppm to 30 ppm after a 480-day period. The Oregon State work in progress thus provides strong support to the adequacy of the soil surface application as a disposal method for concentrated 2,4-D wastes.

Option #4 - Deep-Well. Although 2,4-D is only sparingly soluble in water, its persistence and stability in water and the potential contamination of ground water make deep-well at best a questionable method for the disposal of 2,4-D. Incidents of ground water contamination that persisted for over 3 years leading to the damage of lawns, shrubs and crops, as a result of the penetration of the 2,4-D waste water through permeable sediments after being discharged to rivers or lagoons have been reported.[446] Deep-well disposal of 2,4-D wastes is currently being practiced at Dow Chemical Company, Midland, Michigan,[1778] but the method is not recommended by the National Working Group on Pesticides,[620] and should be considered only under very special situations where hazards would be nonexistent.

The disposal of 2,4-D wastes in open pits, lagoons, unapproved landfill sites, and by on site burning or deep sea burial are not recommended practices because of the obvious contributions to air and water pollution.

To summarize, the adequate methods for treating dilute 2,4-D wastes are: (1) adsorption with powdered activated carbon; (2) adsorption with granular activated-carbon beds; (3) biological degradation; and (4) ion exchange.

The adequate methods for the disposal of concentrated 2,4-D wastes are (1) incineration, and (2) soil surface application.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that disposal systems to handle both dilute and concentrated 2,4-D will still be required at National Disposal Sites located near formulators, users, and especially agriculture centers in the near future. The dilute 2,4-D wastes that will require treatment include spent cleaning solutions for 2,4-D containers and any other 2,4-D contaminated waste water. The concentrated 2,4-D wastes that will require treatment include any surplus, contaminated, partially or fully degraded pesticides.

The processes recommended for the treatment of dilute 2,4-D wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Activated-Carbon Beds	First Choice	Demonstrated technology on commercial scale; also adequate for removal of the sodium salt and esters of 2,4-D and most other types of pesticides from waste water.
Ion Exchange	Second Choice	Demonstrated technology; requires neutralization to the sodium salt first and not adequate for the removal of the 2,4-D esters from water.
Biological Degradation	Third Choice	Demonstrated technology on commercial scale; requires dilution with municipal sewage before treatment in aerated lagoons and stabilization ponds.

The processes for the treatment of concentrated 2,4-D wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Incineration	First Choice	Demonstrated technology; applicable to the disposal of organic pesticide wastes; possibility of recovering chlorine in the form of usable hydrogen chloride.
Soil Surface Application	Second Choice	Demonstrated technology; also applicable to the disposal of other types of herbicides that are degradable by soil microorganisms.

It should be noted that the activated carbon bed and biological degradation processes could also be employed in the treatment of other types of dilute aryloxalkylcarboxylic acid wastes, such as 2,4,5-T and MCPA wastes. To dispose of other types of concentrated arloxalkylcarboxylic acid wastes, because of the lack of supporting data on soil surface application, incineration is the only recommended process.

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HM 135

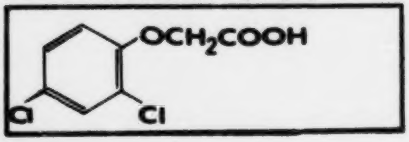
HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name 2,4-D

IUC Name 2,4-Dichlorophenoxyacetic acid

Common Names

Structural Formula



Molecular Wt.[1] 221.05 Melting Pt.[2] 138-140C(1) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

0.4 mm @ 160C(2) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.06% at 25C Hot Water Ethanol

Others: Highly soluble in ether, benzene, carbon tetrachloride, acetone, and tetra and pentachloroethanes(2)

Acid, Base Properties A typical organic acid that readily forms sodium, potassium, and ammonia salts.

Highly Reactive with

Compatible with

Shipped in fiber drums and bags.

ICC Classification Coast Guard Classification

Comments 2,4-D is a white crystalline substance when pure and has practically no odor; the technical grade compound, however, smells more or less like dichlorophenol.(2)

References (1) 509, p.36
(2) 1618, p.163
(3)

[1] Give a reference for each entry.

[2] Supply units where necessary

Table 1. Equilibrium Composition of 2, 4-D/Air System (1 ATM Pressure) Mole Fraction, Gas Phase

Wt % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCl	HCN	N_2	Condensed Phase Graphite Mol/ 100 G Feed
100	1200 C	2.329-4	4.283-1	1.574-4	2.852-1	2.580-4	2.859-1	-	-	2.575
	800 C	3.522-3	3.883-1	2.151-2	2.758-1	1.400-2	2.967-1		-	2.667
	500 C	4.171-2	2.812-2	1.982-1	1.373-1	1.870-1	4.077-1	-	-	3.297
70	1200 C	1.002-4	4.010-1	1.380-4	1.870-1	1.585-4	1.875-1	2.671-4	2.238-1	1.472
	800 C	1.520-3	3.661-1	1.912-2	1.812-1	8.671-3	1.930-1	-	2.304-1	1.558
	500 C	1.832-2	2.772-2	1.925-1	9.099-2	1.222-1	2.499-1	-	2.983-1	2.213
50	1200 C	-	3.820-1	1.253-4	1.189-1	1.000-4	1.192-1	2.772-4	3.794-1	0.554
	800 C	6.167-4	3.508-1	1.756-2	1.154-1	5.292-3	1.220-1	-	3.883-1	0.633
	500 C	7.594-3	2.762-2	1.911-1	5.858-2	7.836-2	1.522-1	-	4.845-1	1.293
20	1200 C	-	7.792-2	1.560-1	8.168-3	4.322-2	5.198-2	-	6.621-1	-
	800 C	-	7.012-2	1.638-1	1.656-2	3.543-2	5.199-2	-	6.621-1	-
	500 C	1.045-3	2.771-2	1.924-1	2.173-2	2.916-2	5.300-2	-	6.750-1	0.056

The data format used is an exponential form, i.e. X.XX-Y is equivalent to $X.XX10^{-Y}$
Mole fractions less than 10^{-4} are indicated by -.

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PROFILE REPORT

Dinitro Cresol (162)

1. GENERAL

Introduction

Dinitro cresol (4,6-dinitro-o-cresol, DNOC) belongs to the class of dinitrophenol compounds with a wide range of biocidal action and are useful as insecticides, acaricides, herbicides, and fungicides. Potassium dinitro-o-cresylate, marketed in Germany in 1892, was the first synthetic organic insecticide. The compounds in use today are all derivatives of 4,6-dinitro-2-alkylphenols and their salts or esters.

Current production of DNOC is only at the rate of 20,000 to 30,000 lb/year,[1964] and indications are that it is being displaced more and more by its homologs, and primarily by 2,4-dinitro-6-sec-butylphenol (DNBP, dinoseb). DNBP has the advantages of being less explosive, somewhat less toxic to man and domestic animals, and more effective in controlling plant pests, plant diseases, and weeds. DNBP surpasses DNOC almost three times in insecticidal and herbicidal effect, and because of the lower dosage, the cost of treatment per unit of area is substantially lower. Less of the DNBP compound remains on the plants, and the hazard in using it is decreased. Although the present profile report is principally concerned with DNOC, the waste management techniques discussed will also be generally applicable to DNBP.

Manufacture

DNOC is produced by the direct nitration of o-cresol with a nitrating mixture at a low temperature, or in some cases, the o-cresol is first sulfonated with concentrated sulfuric acid before the nitration.

Blue Spruce Company, Basking Ridge, New Jersey, is the only U.S. manufacturer of technical grade DNOC.[1964]

Uses

DNOC is used in agriculture to control plant pests and diseases, and for the treatment of fruit trees before opening of the buds, either in the form of emulsions with oils or more often in the form of aqueous solutions of its salts. In the control of weeds DNOC is used exclusively in the form of aqueous solutions of the salts, and good results are obtained in weed control in plantings of flax, grains, and some other crops.[1618]

Sources and Types of Pesticide Wastes

The sources of pesticide wastes may include the following[0620]: (1) pesticide manufacturers; (2) pesticide formulators; (3) pesticide wholesalers; (4) professional applicators; (5) cooperage facilities that recondition drums; (6) agricultural users; (7) government facilities that store, transport, and use pesticides; (8) urban and suburban home garden users; (9) commercial and industrial processes including those from rug and fabric treatment facilities manufacturing plants, hospitals, etc.

In general, pesticide wastes can be classified as either diluted or concentrated wastes. Diluted pesticide wastes include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent caustic solutions used to clean empty pesticide containers. Concentrated pesticide wastes include any unused or contaminated pesticides, pesticide materials left in containers after emptying, sludges formed in treating waste water containing pesticides, sawdust or straw used to soak up accidental pesticide spills.

Physical and Chemical Properties

The physical and chemical properties of DNOC are described in the attached worksheet.

2. TOXICOLOGY

The dinitrophenols are biologically active because of their ability to uncouple oxidative phosphorylation. As a result insects poisoned by DNOC undergo pronounced increases in the rate of respiration, which may reach 3 to 10 times normal, and they die from metabolic exhaustion because of their inability to utilize the energy provided by respiration and glycosis for the conversion of ortho-phosphate to high energy phosphate bonds.[0509]

DNOC is also highly toxic to man and animals and a number of fatalities have resulted from its use in medicine, industry, and agriculture. It is an accumulative poison in man and is excreted very slowly. The symptoms of poisoning include a feeling of warmth, excessive perspiration and thirst, general debility and weariness, acute distress, collapse, and death followed by almost instantaneous rigor. Opacity of the lens of the eye has been produced in laboratory animals following chronic poisoning by DNOC and has occurred occasionally in humans taking this compound for reducing purposes in the past.[1617]

The acute oral and dermal LD_{50} values of DNOC to the rat are 30 and 600 mg/kg body weight respectively.[1277] The chronic toxicity of DNOC has also been extensively studied, and it was established that a DNOC concentration of 100 ppm can be tolerated in the diet with no measurable effects.[0509,1617]

The American Conference of Governmental Industrial Hygienists (ACGIH) 1971 recommended Threshold Limit Value (TLV) for DNOC in air is 0.2 mg/M^3.[0225]

The 48-hr Median Tolerance Limits (TL_m) for DNOC established by the Federal Water Pollution Control Administration for various types of fresh water organisms in micrograms per liter are[0509]: P. Californica (stream invertebrate), 560; and Rainbow trout (fish), 210. These data are indicative of the hazards to aquatic life associated with the use of DNOC.

3. OTHER HAZARDS

DNOC forms highly water soluble salts with caustic alkalies, ammonia, and organic amines, and these salts when in the dry state explode readily from shock or detonation.[1618]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

DNOC is highly toxic and is rapidly absorbed through the intact skin when used in the form of oil solutions. Work with DNOC should be carried out with the strict observance of necessary precautionary measures, and the use of rubber gloves, goggles, a respirator, and other protective clothing is advisable. Special care should be exercised in handling the salts of DNOC because of their explosive nature.

DNOC should be stored in cool, dry, well ventilated places and away from any area where the fire hazard may be acute. Outside or detached storage is preferred. Proper warning signs should be posted in storage areas.[1616]

DNOC is classified as a Class B poison by the Department of Transportation and the rules governing its transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 71-90.[0278]

The National Agricultural Chemicals Association has established a Pesticide Safety Team Network with Area Coordinators throughout the country to provide nationwide 24-hr service. The network became operational on March 9, 1970 (with a central telephone number [513] 916-4300) and should be consulted in all cases of accidents, spills, leakage, fires, and other types of disasters involving DNOC.

Disposal/Reuse

Contaminated or degraded DNOC could not be practically considered for reprocessing. The safe disposal of the pesticide is defined in terms of the recommended maximum concentrations released to the atmosphere and a potable water source and/or marine habitat. These recommended maximum concentrations are as follows:

Contaminant & Environment	Maximum Concentration & Point Source Release Rate	Basis for Recommendation
DNOC in air	0.002 mg/M^3/2 4 hours	0.01 TLV
DNOC in water	2.1 μg/liter	0.01 48-hour TL_m for fish life

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Dilute Pesticide Wastes

Option No.1 - Adsorption with Granular Activated-Carbon Beds. Treatment of waste water containing DNOC with activated-carbon columns has been practiced by Fisons Pest Control Ltd., in England since 1955,[1035,1631] where over 99 percent removal of the pesticide is obtained. There are six adsorption towers, each 7 ft 6 in. in diameter and 25 ft high overall, capable of containing 7 to 10 tons of activated carbon. The activated carbon employed is normally 10 to 20 B.S.S. mesh and the flow rate through the towers normally 3,000 gal/hr, and the spent carbon is reactivated in a conventional rotary furnace. The nominal concentrations of DNOC in the plant effluent are 60 to 190 ppm before treatment and 0.1 to 0.6 ppm after treatment. The treated effluent is diluted with river water before additional treatment in trickling filters and an aeration system followed by discharge to river. No further removal of DNOC from the waste water is observed in the biological treatment stages, but the results of governmental biological surveys indicated no effects of the discharge on the river thus indicating the adequacy of the activated-carbon treatment by itself. Because of the proven capability and the fact that it is a well established chemical engineering unit operating, adsorption with granual activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute DNOC wastes.

Option No. 2 - Adsorption with Powdered Activated Carbon. Although the use of powdered activated carbon to remove DNOC from water has not been investigated directly, the effectiveness of DNOC adsorption with granular activated-carbon beds and the results of the related studies on powdered activated carbon adsorption of other pesticides conducted by Robeck et al,[441] Sigworth,[1635] and Whitehouse[0445] indicate that the addition of powdered activated carbon to a liquid solution followed by stirring and filtration is an adequate method for treating dilute DNOC wastes.

Option No. 3 - Biological Degradation. Southern Dyestuff Company, Charlotte, North Carolina, has demonstrated on the pilot plant scale that waste waters containing nitrophenols could be successfully treated in an activated sludge unit,[1450] and is presently in the process of installing a complete waste treatment facility including an activated sludge unit, an aeration system, and a chlorination stage to handle their manufacturing waste streams.[1805] In the opinion of Southern Dyestuff, waste waters containing DNOC could also be adequately treated by the same system.[1805]

Option No. 4 - Eli Lilly Process. R. H. L. Howe of Eli Lilly and Company has developed a patented process for removing nitrophenols and nitroanilines from waste waters.[0534] The process consists of acidifying the waste stream to a pH of less than about three, adding an absorbent material to take up the colored components, adding a metallic oxide or hydroxide to adjust the pH to more than about five and also to form a precipitate, and separating the mixture into an effluent and a sludge or foam (scum). The resulted effluent is free of nitrophenols and nitroanilines and can then be treated by conventional techniques. According to Howe,[1802, 1974] the process is also applicable to the treatment of waste waters containing 100 ppm to a few weight percent DNOC, and the treated effluent would be non-toxic to fish life and safe to any receiving sewer or water course.

Option No. 5 - Light Catalyzed Chlorine Oxidation. The effect of ultraviolet radiation on the rate and extent of chlorine oxidation of 2,4-dinitrophenol has been briefly investigated by Meiners et al.[0887,1804] The results with initially 38 ppm 2,4-dinitrophenol (15 ppm total organic carbon) indicated the rapid degradation of the compound (practically 100 percent elimination in 8 min) and the fairly rapid decrease in the total organic carbon (53 percent in 10 min), and demonstrated the value of the process as a near future treatment method for dilute DNOC wastes.

Concentrated Pesticide Wastes

Option No. 1 - Incineration. The complete and controlled high temperature oxidation of DNOC in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of the pesticide. The research on incineration of pesticides conducted by Kennedy et al at Mississippi State University has led to the conclusion that DNBP approached complete combustion at temperatures as low as 600 C and identified carbon monoxide, carbon dioxide, and ammonia as the volatile products from burning of the DNBP formulation at 900 C.[0062,0063] Because of the similarity in chemical structure of DNBP and DNOC, temperatures not far above 600 C should also be sufficient to degrade DNOC and the same combustion products should be obtained. Properly designed and operated incineration is therefore considered as the best present and near future method for the disposal of concentrated DNOC wastes.

Option No. 2 - Chemical Degradation. The use of chemical reagents to decompose concentrated pesticide wastes to less toxic forms has also been investigated by Kennedy et al.[0062,0063] The Mississippi State work showed that: (1) DNBP was altered structurally by sodium hydroxide but the spectrum produced was not resolved; (2) 80 percent of the DNBP were decomposed when treated with the sodium biphenyl reagent prepared by heating a mixture of metallic sodium, anhydrous toluene, and the dimethyl ether of ethylene glycol; (3) 93.8 percent DNBP degradation were obtained when the pesticide was treated with liquid ammonia and metallic sodium. Although liquid ammonia and metallic sodium would probably also completely decompose DNOC, the reagent is dangerous to use and the toxicity of the degradation products are not known. Based on the results to date, chemical degradation could not be recommended as a method for the disposal of concentrated DNOC wastes.

Option No. 3 - Sanitary Landfill. Although data is not available on the persistence of DNOC in soil, the pesticide readily forms water soluble ammonium, sodium, potassium, and calcium salts and poses the problem of potential ground and surface water pollution. Sanitary landfill should therefore be considered only for the disposal of small quantities of DNOC wastes, and only at approved sites that are acceptable from a geologic and ground water hydrology standpoint.[0620]

Option No. 4 - Deep-Well. Although DNOC itself is only sparingly soluble in water, the potential contamination of ground water by the water soluble ammonium, potassium, sodium, and calcium salts of DNOC makes deep-well, at best, a questionable method for the disposal of DNOC. Deep-well disposal is not recommended by the National Working Group on Pesticides,[0620] and should be considered only under special situations where hazards would be nonexistent.

The disposal of DNOC wastes in open pits, lagoons, unapproved landfill sites, and by onsite burnings or deep-sea burial are not recommended practices because of the obvious contributions to air and water pollution.

To summarize, the adequate methods for treating dilute DNOC wastes are either adsorption with granular activated-carbon beds or adsorption with powdered activated carbon. The only adequate method for the disposal of concentrated DNOC wastes is incineration. Based on the information to date, activated sludge treatment, the Eli Lilly process, and light catalyzed chlorine oxidation could all be considered only as possible near future methods for treating dilute DNOC wastes.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The declining demand for DNOC indicates that it is probably not a likely candidate for a National Disposal Site in the future. However, the treatment facilities used to dispose of other types of pesticide wastes at National Disposal Sites are generally also adequate to handle DNOC wastes. In particular, the recommended unit operations at National Disposal Sites for pesticide disposal--activated-carbon beds and incineration--are also the preferred processes for treating dilute and concentrated DNOC or other types of dinitrophenol wastes.

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H.M. 162

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Dinitro Cresol

IUC Name 2-4-dinitro-6-methylphenol

Common Names 4,6-dinitro-O-cresol, DNC, DNOC

Structural Formula

Molecular Wt.[1] 198.1 Melting Pt.[2] 86.4C(2) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

5.2 X 10^{-5}mm@ 25 C(2) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.0128%(2) Hot Water Ethanol 4.3% at 15 C(3)

Others: very soluble in acetone and benzene

Acid, Base Properties DNOC is a pseudo acid and readily forms water soluble sodium, potassium, calcium and ammonium salts(1)

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B Coast Guard Classification

Comments DNOC is a yellow crystalline substance in the pure state.

References (1) 509, p. 79
1618, p. 97
(2) 1433, p. 689
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

PROFILE REPORT ON
HALOGENATED ALIPHATIC HYDROCARBON FUMIGANTS
Ethylene Bromide (182), Methyl Bromide (267), Methyl Chloride (268)

1. GENERAL

Introduction

Fumigants are chemicals which are distributed through space as gases, and, therefore,at a given temperature and pressure must exist in the gaseous state in sufficient concentraction to be lethal to the insect pest. This physical requirement greatly limits the number of insecticides which may be used as fumigants, and most of the fumigants marketed today are halogenated hydrocarbons with high vapor pressures. Methyl bromide is one of the most widely used general fumigants, and ethylene bromide (ethylene dibromide) is an effective soil fumigant because of its slower release rate of vapors. Methyl chloride, though not mainly used as a fumigant, is often employed in aerosol bombs to control flying insects in enclosed premises.

The 1970 production figures for the three fumigants are: ethylene bromide, 296,826,000 lb; methyl bromide, 21,047,000 lb; and methyl chloride, 422,678,000 lb.[1718] All three commodities are expected to sustain a moderate to good growth rate in the near future, despite the fact that ethylene bromide is also used as a component of antiknock fluid in conjunction with lead alkyls and the possible phasing out of leaded gasoline.[1506]

Manufacture

Ethylene Bromide. Ethylene bromide is manufactured by reacting ethylene and bromine in either batch or continuous processes, with the final product obtained after washing the reactor effluent with dilute aqueous alkali to remove small quantities of hydrogen bromide followed by fractional distillation.[1808] The U.S. producers of ethylene bromide include the following[1506,1966]:

Dow Chemical Company, Midland, Michigan.
Ethyl Corp., Bromet, Arkansas.
Ethyl Corp., Houston, Texas.
Great Lakes Chemical Corp., El Dorado, Arkansas.
Houston Chemical Co., Beaumont, Texas.
Michigan Chemical Corp., El Dorado, Arkansas.

Methyl Bromide. Methyl bromide is usually manufactured by using elementary bromine together with a reducing agent as the source of hydrogen bromide for reaction with methanol. The reducing agents that have been employed include sulfur dioxide, hydrogen sulfide, and sulfur raw oil, and both batch and continuous processes have been carried out industrially.[1808] The current U.S. producers of methyl bromide are [1506,1818]:

Dow Chemical Co., Midland, Michigan
Great Lakes Chemical Corp., El Dorado, Arkansas.
Kerr-McGee Chemical Corp., Los Angeles, California.
Michigan Chemical Corp., St. Louis, Michigan.

Methyl Chloride. The two principal processes for industrial production of methyl chloride are chlorination of methane and reaction of hydrogen chloride with methanol. The methanol-hydrogen chloride reaction yields methyl chloride as the sole product, whereas chlorination of methane yields other chlorinated hydrocarbon coproducts of equal commercial importance in substantial amounts, such as methylene chloride and carbon tetrachloride. The U.S. producers of methyl chloride include the following[1506,1718]:

Allied Chemical Corp., Moundsville, West Virginia.
Ancon Chemical Corp., West Lake, Louisiana.
Dow Chemical Co., Freeport, Texas.
Dow Chemical Co., Pittsburgh, California.
Dow Corning Corp., Carrollton, Kentucky.
Dow Corning Corp., Midland, Michigan.
E. I. Du Pont de Nemours & Co., Niagara Falls, New York.
Ethyl Corp., Baton Rouge, Louisiana.
Vulcan Materials Co., Chemical Division, Newark, New Jersey.
Union Carbide Corp., Institute, West Virginia.

Uses

Ethylene bromide is used mostly as an ingredient of automobile and aircraft fuels to aid in removing lead from the engine cyclinders. The next most important use is an active ingredient of grain fumigant formulations for insect control and of soil fumigants for the control of wireworms and nematodes. Other much smaller uses are as a nonflammable solvent for resins, gums, and waxes, and as an intermediate in synthesis.[1433]

The major use of methyl bromide is in the extermination of insect and rodent pests, as the compound is very suitable for the fumigation of food commodities and areas in which they are processed and stored, as well as for tobacco and other kinds of nursery stock. Methyl bromide has also been used as a fire extinguisher, although its application is limited due to its high toxicity. In moderately small amounts, methyl bromide is used in organic synthesis, particularly as a methylating agent.[1433]

The principal uses of methyl chloride are in the manufacture of silicons, butyl rubber, tetramethyl lead, and methyl cellulose. Methyl chloride is also used as a fumigant in controlling flies and other flying insects, but the application in this area amounts to a small proportion of its total usage. Other industrial applications include its use as a methylating agent in the production of quaternary ammonium compounds and of triptane, and as starting material in the manufacture of methylene chloride, chloroform, carbon tetrachloride, and of various bromochloro- and chlrofluoro-methanes.[1433]

Sources and Types of Wastes

The sources of ethylene bromide, methyl bromide, and methyl chloride wastes may include the following: (1) manufacturers of the chemicals; (2) pesticide formulators; (3) wholesalers of the chemicals; (4) professional applicators; (5) cooperage facilities that recondition drums; (6) agricultural users; (7) government facilities that store, transport, and use the chemicals; (8) urban and suburban home and garden users; (9) commercial and industrial processes utilizing these chemicals--gasoline formulation in the case of ethylene bromide and silicone, butyl rubber, tetramethyl lead and methyl cellulose manufacturers in the case of methyl chloride.

In general, ethylene bromide, methyl bromide, and methyl chloride wastes can be classified as either diluted or concentrated wastes. Diluted aqueous wastes include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent cleaning solutions for the empty containers. Diluted gaseous wastes include gas streams in the manufacture of other products that require purification and removal of these toxic halohydrocarbons, and also any gas streams released to the atmosphere containing these compounds. Concentrated wastes normally include any unused or contaminated chemicals, and materials left in containers after emptying.

Physical and Chemical Properties

The physical and chemical properties of ethylene bromide, methyl bromide and methyl chloride are summarized in the attached worksheets.

2. TOXICOLOGY

Ethylene bromide is highly toxic to man and animals, and is readily absorbed through lungs, intact skins, and the gastrointestinal tract. Continued exposure to low doses causes irritation of the eyes, nose, respiratory tract, and finally paralysis of the hind legs from which the animal may recover eventually. Through errors in labeling, it has been used occasionally in place of ethyl bromide in anesthesia, leading to cases of fatal poisoning as a result of cardiac failure. Contact with the skin may cause injury with blister formation.[1808]

Methyl bromide is a highly toxic substance of insidious action. Single exposures to 1,000 ppm for 30 to 60 minutes are dangerous to life. The effects are on both respiratory and central nervous system, although death is usually caused by lung irritation resulting in congestion and edema. The early symptoms of fatal poisoning are headache, visual disturbances, nauses and vomiting, smarting of the eyes, irritation of the skin, listlessness, vertigo, and tremor. Exposure to concentrations as low as 100 to 500 ppm over a period of time may lead to chronic poisoning, resulting in a variety of symptoms and signs, most of which are due to injury of the central nervous system and include blurred or double vision, slurred speech, numbness of the extremities, mental confusion, hallucinations, tremor, coma, or frequent fainting attacks. Recovery is often prolonged and there may be permanent injury, such as sensory disturbances, weakness, disturbances of guilt,irritability, and blurred vision. In addition, liquid methyl bromide is an extreme irritant to the skin and may produce severe burns.[1301,1810]

Methyl chloride is a dangerous anesthetic and narcotic, about one-fourth as active as chloroform, and presents serious problems to life and health when inhaled in high concentrations. Poisoning by methyl chloride produces the following characteristic symptoms: drowsiness, mental confusion, coma, nausea, vomiting, and in severe cases, convulsions and death. It is dangerous in that after apparent recovery from seemingly mild exposures, serious and sometimes fatal return of symptoms may occur even afterafter an interval of several days. It is absorbed quickly but eliminated rather slowly, and for this reason repeated exposures are hazardous. Recovery after what may appear to be a relatively slight exposure may be delayed 2 to 3 weeks, and after severe exposure some effects on the nervous system may be present for months or even years. Severe exposure may also effect the liver, kidneys, and blood forming tissues, lead to an increase in pulse rate, temperature, and breathing rate. Acute poisoning of methyl chloride is relatively rare, but might occur with exposures to well over 500 ppm. The type of poisoning occuring most frequently is due to repeated exposure to concentrations less than 500 ppm. Although methyl chloride is in its vapor state at ordinary temperatures and will produce little or no local effect, a stream of concentrated vapor striking the skin may result in a condition resembling frost bite followed by reddening, and occasionally, blister formation.[1301,1811]

The American Conference of Governmental Industrial Hygienists 1971 recommended Threshold Limit Values (TLV) for these compounds in air are[0025]: ethylene bromide, 25 ppm or 190 mg/M^3; methyl bromide, 20 ppm or 80 mg/M^3; and methyl chloride, 100 ppm or 210 mg/M^3.

Because of their volatility, the water pollution hazards arising from the human toxicity of methyl bromide and methyl chloride are relatively slight. For ethylene bromide, the approximate lethal dose to man has been estimated to be 65 mg/kg body weight.[1312]

No actual published data of aquatic toxicity for the three compounds were found. However, the National Research Council's Committee on Hazardous Materials, based on the physical properties of these compounds and their chemical similarity to other chemicals of known toxicity, has given a Grade 3 aquatic toxicity rating to ethylene bromide and a Grade 1 aquatic toxicity rating to methyl bromide and methyl chloride.[0311] Although a Grade 3 rating normally indicates a threshold range of 1 to 100 ppm to aquatic life and a Grade 1 rating a threshold range of 1,000 to 10,000 ppm to aquatic life, these ratings were also modified in some cases for chemicals having low water solubility or high volatility to account for the lower probability of water pollution, and this explains the low aquatic toxicity ratings given to methyl bromide and methyl chloride.

3. OTHER HAZARDS

Ethylene bromide is a nonflammable liquid, but reacts vigorously with metals such as aluminum, magnesium, sodium and potassium, strong alkalies, and oxidizing agents.[96] An explosion may result if a mixture of liquid ammonia and ethylene bromide is allowed to warm up to room temperature.[1433]

At atompsheric pressure methyl bromide is practically nonflammable. Methyl bromide is also not particularly corrosive to most metals, although it attacks aluminum and magnesium and their alloys. With aluminum, methyl bromide forms the spontaneously ignitable aluminum trimethyl.[1810]

Methyl chloride is thermally stable, but may breakdown to produce hydrogen chloride and other toxic gases at high temperatures. It hydrolyzes slowly in water or upon contact with moisture, with the formation of hydrochloric acid, and is therefore corrosive. In addition, the hydrochloric acid formed attacks most metals with the evolution of hydrogen, which may form explosive mixtures with air. When dry, methyl chloride is inert towards most engineering materials except zinc, aluminum, magnesium, and their alloys. However, once reaction of methyl chloride with these metals or alloys initiates, it is greatly accelerated by the reaction products, resulting in rapidly increasing pressure if confined, and the release of gases which may ignite spontaneously.[1811]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Ethylene bromide, methyl bromide, and methyl chloride are all toxic by inhalation or skin contact. Full protective clothing and the use of a respirator are recommended in their handling and application. In cases of accidental contact, all contaminated clothing should be removed immediately and the skin washed thoroughly with soap and water.[0096,1810,1811]

Storage of these chemicals should be in cool, dry, well-ventilated areas, away from acute fire hazards. Because of their low boiling points, containers or storage vessels of methyl bromide and methyl chloride should also be protected from excessive heat and against sudden rise in temperatures.[1810,1811]

Methyl bromide is classified by the U.S. Department of Transportation (DOT) as a Poisonous Liquid, Class B, and methyl chloride is classified by DOT as a Flammable Compressed Gas. As such, both chemicals must be packed in DOT specification containers when shipped by rail, water, or highway and all DOT regulations governing loading, handling, shipping, and labeling must be complied with. Ethylene bromide is not classified by DOT, but due to its toxic nature, the same regulations governing the handling, loading, and shipping of Class B Poisonous Liquids should also be followed here.

Additional information on the safe handling and use of methyl bromide and methyl chloride are described in greater detail in the Chemical Safety Data Sheets SD-35 and SD-40 published by the Manufacturing Chemists Association.

Disposal/Reuse

Contaminated or degraded ethylene bromide, methyl bromide and methyl chloride are usually not considered for reprocessing, although manufacturers would normally accept these for disposal. The safe disposal of ethylene bromide, methyl bromide, or methyl chloride is normally defined in terms of the recommended maximum concentrations released to the atmosphere:

Contaminant in Air	Recommended Maximum Concentration	Basis for Recommendation
Ethylene bromide	1.9 mg/M^3/24 hr	0.01 TLV
Methyl bromide	0.8 mg/M^3/24 hr	"
Methyl chloride	2.1 mg/M^3/24 hr	"

Based on the Grade 3 aquatic toxicity rating by the National Research Council's Committee on Hazardous Materials,[0311] the recommended maximum concentration of ethylene bromide in water is 1 ppm. No water quality standards are recommended for methyl bromide and methyl chloride, as they are both highly volatile and unlikely to pose a water pollution hazard.

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL/RECOVERY PROCESSES

Ethylene bromide, methyl bromide and methyl chloride generally do not present pollution problems to the chemical industry and very few specific efforts have been made to study their control or disposal. For these reasons, most of the removal, disposal, or recovery techniques discussed here are near future processes where no quantitative data are available.

Removal from Air

Option No. 1 - Refrigerated Condensation. When present in sufficiently high concentrations, refrigerated condensation has been used and is the recommended method for removing ethylene bromide, methyl bromide, or methyl chloride from air or a gas stream.[1965,1966,1972,1986] The halohydrocarbons are almost completely recovered, and the remaining traces can be removed by the other processes described here.

Option No. 2 - Monoethanolamine Scrubbing. Monoethanolamine (MEA) is commonly used for the removal of acid gases (hydrogen sulfide and carbon dioxide) in scrubbing towers. The absorption of ethylene bromide and methyl bromide by MEA has been used in the analytical determination of these compounds in air.[2029,2031] This indicates that MEA scrubbing could also be conceivably employed in removing these compounds from air on the commercial scale, although it remains to be demonstrated that the fouled MEA could be readily regenerated by methods such as steam stripping.

Option No. 3 - Alkaline Alkoxide Scrubbing. Ethylene bromide, methyl bromide, and methyl chloride could all be readily absorbed from the air by scrubbing with a solution of potassium or sodium hydroxide in anhydrous methanol and ethanol.[1301,2032] In the case of ethylene bromide, vinyl bromide is immediately formed, although further dehalogenation occurs very slowly in the alcoholic solution.[2030] For methyl bromide and methyl chloride, either the dimethyl ether or the methyl ethyl ether is formed, depending on whether methanol or ethanol is used in the absorbent. In fact, the reaction between alkyl halides and alkali alkoxides is the well-known Williamson ether synthesis and provides a method of preparing symmetrical and unsymmetrical ethers.[1808] The time required to reach 100 percent conversion of a known amount of methyl bromide in a potassium hydroxide-methanol solution at different temperatures has been measured and reported by Dumas and Latimer,[2032] and their results showed that complete conversion was obtained in 7 hr at 24 C or only 45 min at 70 C with 1N potassium hydroxide in methanol. However, similar experiments have not been conducted with either methyl chloride or ethylene bromide, and the effectiveness of alkali alkoxides as an absorbent for the alkyl halides on the commercial scale has yet to be proven.

Option No. 4 - Alcohol Scrubbing. Dow has experimented with the use of methanol scrubbing for the removal of methyl bromide from air, but to date only marginal results are obtained for the low methyl bromide concentration ranges (0.1%) investigated.[1969] When higher concentrations of methyl bromide in the air are encountered, however, Dow believes methanol scrubbing would be an effective means to achieve a high rate of removal. Ethylene bromide has also been reported to be readily absorbed from air by shaking with ethyl alcohol,[2030] but again,data are not available to determine the applicability of the process on commercial scale.

Option No. 5 - Adsorption with Activated Carbon. Activated carbon is extensively employed for the removal of traces of gas impurities from air and it has been suggested that small quantities of ethylene bromide, methyl bromide, or methyl chloride could be effectively removed from air by passage through activated-carbon traps or beds.[1986,1987]

Removal from Water

Ethylene bromide is only slightly soluble in water and most if it can be removed from water in a gravity separator or a settling pond due to its density that is more than twice that of the water.[1965,1967] Methyl bromide is practically insoluble in water and is also extremely volatile, and hence does not contribute to water pollution. Methyl chloride is slightly soluble in water but again is also very volatile and can be readily removed from water by simple physical methods. Some of the techniques used for treating water contaminated with these compounds are described below briefly.

Option No. 1 - Steam Stripping. Steam stripping is a widely used disposal method in the chemical and petrochemical industry and can be used to remove ethylene bromide, methyl bromide, or methyl chloride from water.[1970,1972,1987] The waste gases from stripping must be burned in incinerators equipped with adequate scrubbing to totally prevent air pollution.

Option No. 2- Blowing with Air. The Manufacturing Chemists Association recommends removing methyl chloride from water by blowing the contaminated water with air, and burning the outlet air stream in cases of gross contamination, with a flash arrestor on the vent line.[1811] Air blowing can also be used in removing the equally volatile methyle bromide from water.

Option No. 3 - Adsorption with Activated Carbon. The engineering firm of Camp, Dresser, and McGee has completed a pilot scale investigation on the use of both powdered and granular activated carbon for the removal of chlorinated hydrocarbons from the combined waste waters of several chemical plants in the Niagara Falls, New York area, including the Du Pont facility there that manufactures methyl chloride.[1971,1992] Although the removal of any of the individual compounds was not separately studied, the pilot work was considered a success and Camp, Dresser, and McGee is currently designing a full scale physical-chemical waste treatment facility to serve the industrial concerns in the area. It has also been claimed that activated carbon can be used to remove traces of ethylene bromide from water.[1968] However, activated carbon treatment is of value mainly for the adsorption of organic compounds of relatively high molecular weight and its effectiveness in removing ethylene bromide or methyl chloride from water requires further investigation.

In addition, because of the volatility of methyl bromide and methyl chloride, adequate treatment of waste waters contaminated with small quantities of these compounds could probably be achieved in conventional municipal facilities with aeration.

Disposal/Recovery of Concentrated Wastes

Option No. 1 - Incineration. The complete and controlled high temperature oxidation of halohydrocarbons in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of these compounds with the possibility of recovering the greater part of all of the halogens in some usuable form. In particular, Dow Chemical is currently in the process of designing incinerators to dispose of the concentrated ethylene bromide * and methyl bromide wastes

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* Auxiliary fuel will be required in the combustion of ethylene bromide.

accumulated at its Midland Plant.[1970] The off gas from the incinerator will contain both hydrogen bromide and bromine, both of which are harmful pollutants if released to the atmosphere. The hydrogen bromide can be readily removed by scrubbing with caustic soda, but Dow claims to encounter some problems with bromine removal.[1970] However, it is not clear whether Dow has fully investigated the several methods available for the separation of bromine vapors from air: (1) contacting the air-bromine mixture with moist scrap iron leading to the formation of ferrous bromide; (2) absorption in ammonia solution with the formation of ammonium bromide; (3) absorption in ferrous bromide solution with the formation of ferric bromide; (4) alkaline absorption in which bromine reacts with sodium hydroxide or carbonate to form sodium bromate, sodium bromide, and either water or carbon dioxide; (5) lime absorption in which bromine reacts with calcium hydroxide to form calcium bromide and bromate; (6) reduction of bromine by means of sulfur dioxide giving rise to the formation of a spray of fine droplets of hydrobromic and sulfuric acids that could later be trapped by a solution of the same mixed acid circuling in an absorption tower; and (7) absorption with a concentrated solution of sodium bromide cooled below OC in packed towers.[1808] The absorbed bromine that is bound chemically in the form of bromide, bromate or hydrogen bromide can all be recovered by either acidification with sulfuric acid or reoxidizing with chlorine. In the case of methyl chloride, combustion units designed for the disposal of chlorinated organic wastes and capable of recovering chlorine in the form of usable hydrogen chloride have been developed, and a 7000 lb/hr plant is now under construction for E. I. Du Pont de Nemours & Co. in Victoria, Texas by Union Carbide Corp.[1743] Properly designed and operated incineration is therefore considered as the best current and near future method for the disposal of concentrated ethylene bromide, methyl bromide, and methyl chloride wastes.

Option NO. 2 - Chemical Degradation. The use of chemical reagents to decompose concentrated ethylene bromide, methyl bromide or methyl chloride wastes to less toxic forms has not been specifically reported in the literature. Based on the known reactions of these compounds, however, it appears that: (1) metal alkoxides could be used to react with methyl bromide or methyl chloride leading to the formation of ethers and metallic bromides or chlorides according to the Williamson ether synthesis;[1808] (2) sodium in liquid ammonia could be used to react with methyl bromide or methyl chloride leading to the formation of methane, methylamine, and sodium bromide or chloride; and (3) zinc could be added to ethylene bromide with the formation of ethylene and zinc bromide. Since these methods generally do not lead to the recovery of valuable halogens and little is known of the optimum conditions under which the chemical reagents could be applied, chemical degradation could not be recommended as a technique for the disposal of the halohydrocarbons at the present time.

The disposal of ethylene bromide, methyl bromide or methyl chloride wastes in landfill sites, open pits, lagoons and by on site burning, deep-well disposal, or deep sea burial are not recommended practices because of volatility of these compounds and the obvious contributions to air and water pollution.

To summarize, the only demonstrated method for the removal of the halohydrocarbons from air is refriegerated condensation when these compounds are present in sufficiently high concentrations. The use of MEA, alkaline alkoxide and alcohol scrubbing or activated carbon to remove traces of these halohydrocarbons from air seems feasible, but due to the lack of sufficient supporting data could only be considered as near future waste treatment processes. Adequate methods for the removal of the halohydrocarbons from water include steam stripping, and blowing with air in the case of the more volatile methyl bromide and chloride. Again, activated carbon adsorption to remove traces of these compounds from water could not be considered as a proven method. To dispose of concentrated ethylene bromide, methyl bromide, or methyl chloride wastes, the only adequate method is by incineration.

6. APPLICABILITY TO NATIONAL DISPOSAL

It is anticipated that disposal systems to handle dilute ethylene bromide wastes and concentrated ethylene bromide, methyl bromide or methyl chloride wastes will be required at National Disposal Sites. Dilute ethylene bromide wastes requiring treatment will include spent cleaning solutions for ethylene bromide containers and any other waste water contaminated by ethylene bromide. Concentrated ethylene bromide, methyl bromide, or methyl chloride wastes requiring treatment will include any surplus, contaminated, partially or fully degraded compounds.

The process recommended for the removal of ethylene bromide from water is gravity separation followed by steam stripping. To dispose of the concentrated halohydrocarbon wastes, incineration with recovery of the halogens is the only recommended process.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. #182

H. M. Name Ethylene bromide

IUC Name 1,2 -Dibromoethane

Common Names Ethylene dibromide

Structural Formula

$CH_2Br \cdot CH_2Br$

Molecular Wt.[1] 187.88 Melting Pt.[2] 9.3 C (1) Boiling Pt. 131.5 C (1)

Density (Condensed) 2.172 @ 25 C (1) Density (gas) ______ @ ______ ° ______

Vapor Pressure (recommended 55 C and 20 C)

8.5 mm @ 20 C (2) 11 mm @ 25 C (1) 119.9 mm @ 75 C (2)

Flash Point ______ ° Autoignition Temp. ______ °

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water 0.43% @ 30 C (1) Hot Water ______ Ethanol Soluble

Others: Completely miscible with carbon tetrachloride, benzene, gasoline, ether, and anhydrous alcohols. (2)

Acid, Base Properties ______

Highly Reactive with aluminum, magnesium, sodium and potassium, strong alkalies, and oxidizing agents. (3)

Compatible with ______

Shipped in glass bottles, 55-gal drums, tank cars (2)

ICC Classification ______ Coast Guard Classification ______

Comments Ethylene bromide is a clear, colorless liquid with a characteristic sweet odor.

References (1) 1618, p. 38
(2) 1433, V.3, p. 771
(3) ______

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES WORKSHEET

H.M. #267

H. M. Name Methyl Bromide

IUC Name Bromomethane

Common Names

Structural Formula

CH_3Br

Molecular Wt.[1] 94.95 (1) Melting Pt.[2] -93 C (1) Boiling Pt. 3.6 C(1)

Density (Condensed) 1.732 @ 0 C(1) Density (gas) 3.27 @ 0 C (1)
(Air = 1)

Vapor Pressure (recommended 55 C and 20 C)

1250 mm @ 20 C (2) @ ° @ °

Flash Point Practically nonflammable (1) Autoignition Temp. 537 C (1)

Flammability Limits in Air (Vol%) Lower 10.0 Upper 15.4 (1)

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water less than 0.1 wt % (1) Hot Water Ethanol Soluble (1)

Others: Soluble in ethyl ether, carbon tetrachloride, chloroform, carbon disulfide, benzene (1)

Acid, Base Properties

Highly Reactive with aluminium, magnesium, and their alloys (1)

Compatible with

Shipped in metal containers or tank cars (rare) (1)

ICC Classification Poisonous Liquid, class B Coast Guard Classification Poisonous liquid,B

Comments Extremely hazardous liquid and vapor under pressure.

References (1) 1810
(2) 1618, p. 37
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. #268

H. M. Name Methyl Chloride

IUC Name Chloromethane

Common Names

Structural Formula

CH_3Cl

Molecular Wt.[1] 50.491   Melting Pt.[2] -97.6C   Boiling Pt. -23.8C

Density (Condensed) 0.920 @ 20C   Density (gas) (Air = 1) 3.58 @ -15C

Vapor Pressure (recommended 55 C and 20 C)

101 mm Hg @ -80 F   355 6 mm Hg @ -40 F   1093.6mm Hg @ 5 F

Flash Point Below 0 C   Autoignition Temp. 632 C

Flammability Limits in Air (Vol%)   Lower 10.7   Upper 17.4

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water 0.46 wt % at 20 C   Hot Water 0.26 wt % at 40 C   Ethanol soluble

Others: readily soluble in alcohols, chloroform, and mineral oils.

Acid, Base Properties Hydroloyzes in the presence of moisture to hydrochloric acid.

Highly Reactive with aluminum, and to lesser extent with zinc magnesium, the alloys thereof (even when dry), and alkali metals.

Compatible with most other engineering materials.

Shipped in as a liquid under pressure in cylinders and tank cars.

ICC Classification Flammable compressed gas   Coast Guard Classification Inflammable gas

Comments Methyl chloride is thermally stable, but also flammable and subject to decomposition upon contact with moisture. At high temperatures, it may break down to produce hydrogen chloride and other toxic gases.

References (1) 1811
(2)
(3)

[1] Give a reference for each entry.

[2] Supply units where necessary

PROFILE REPORT

Hydrazine (212)

1. GENERAL

Hydrazine is a clear, oily, water-white liquid with an odor similar to that of ammonia. It is a strong reducing agent, weakly alkaline and very hydroscopic. It will react with carbon dioxide and oxygen in air. Exposure of hydrazine to air on a large surface (as on rags) may result in spontaneous ignition from the heat evolved by its oxidation with atmospheric oxygen. With water it forms the diamide hydrate, $H_2NNH_2 . H_2O$.[1300]

Hydrazine is formed by reacting equimolar quantities of sodium hypochlorite and ammonia in an alkaline solution to give chloroamine (NH_2Cl). This reacts at elevated temperature with ammonia to give hydrazine:

$$NH_3 + NaOCl \rightarrow NaOH + NH_2Cl$$

$$NH_3 + NH_2Cl + NaOH \rightarrow N_2H_4 + NaCl + H_2O$$

A side reaction occurs which leads to the decomposition of hydrazine:

$$2NH_2Cl + N_2H_4 \rightarrow N_2 + 2NH_4Cl$$

This side reaction is catalyzed by dissolved chloride. Gelatin, glue, amino acids or simple peptides are added to complex the chlorides.[1157] Hydrazine is recovered from aqueous solution by distilling water until the still bottoms approach the composition of hydrazine hydrate. The hydrate is either treated with sodium hydroxide at a temperature above the boiling point of hydrazine and the hydrazine distilled and collected, or treated with aniline which is used to effect removal of the water by azeotropic distillation.[1433]

Hydrazine is used in jet and rocket fuels, intermediates for agricultural chemicals, antioxidants, textile chemicals, explosives, photographic developers, blowing agents, scavengers for chlorine in hydrogen chloride, corrosion inhibitors and scavengers for oxygen.[1662]

The chemical and physical properties for hydrazine are summarized in the attached work sheet.

2. TOXICOLOGY

Hydrazine is a strong irritant and may damage the eyes and cause respiratory tract irritation. If spilled on the skin or eyes, liquid hydrazine can cause severe local damage or burns and can cause dermatitis. It can penetrate the skin. If inhaled, the vapor causes local (irritation of eye and respiratory tract) and systemic effects. For long exposure, systemic effects involve the central nervous system. On exposure to higher concentrations, convulsions and possibly death follow. Repeated exposures may cause toxic damage to the liver and kidney, as well as anemia.[1300, 1993]

The exposure limits recommended are as follows:[1300]

Threshold limit (ACGIH) -1.0 ppm (1.3 mg/m^3)

Emergency exposure limits -

10 min - 30 ppm (39 mg/m^3)

30 min - 20 ppm (26 mg/m^3)

60 min - 10 ppm (13 mg/m^3)

3. OTHER HAZARDS

Hydrazine is flammable over a broad range of concentrations: 4.7 to 100 percent. It is hypergolic with some oxidants, such as hydrogen peroxide, nitrogen tetroxide, fluorine, halogen fluorides, and nitric acid. A film of hydrazine in contact with metal oxides, such as those of iron, copper, lead, manganese and molybdenum, may ignite owing to the heat of chemical reaction. Hydrazine vapors in a closed system may explode when exposed to air. In the presence of finely-divided or other high surface area forms of some metal or metal oxides, hydrazine dissociates into nitrogen, hydrogen and ammonia.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Adequate procedures for the safe handling, transportation and storage of hydrazine are described in two publications,[1300, 1993] and in the military specification for hydrazine, MIL-P-2705.[1995] Hydrazine is classified by DOT as a corrosive liquid and is shipped under a "White Label." Under DOT specifications hydrazine may be shipped in 1- gallon glass bottles packed in cans, in metal barrels or drums of 304 or 347 stainless steel, or in tank cars of 304L, 347 stainless steel, aluminum 103A AL-W, or aluminum 111A100-W-6.

Hydrazine as a waste will generally be encountered as excess material, as contaminated material from spills, or in aqueous streams from chemical process industries. Because of the hazards involved (unpredictable decomposition), hydrazine is usually not recovered in a concentrated form from contaminated or dilute systems. In ponds or holding tanks dilute hydrazine is decomposed by the air and bacteria into nitrogen, hydrogen, water and ammonia. In a concentrated form, hydrazine is destroyed by burning.

Recommended maximum concentrations of hydrazine in effluent streams released to the environment are as follows:

Containment and Environment	Maximum Concentration at Point Source	Basis for Recommendation
Hydrazine released to the air inside the boundaries of the processing plant.	1.0 ppm	TLV[1300]
Hydrazine released to the air outside the boundaries of the processing plant.	.01 ppm	.01 TLV
Hydrazine released in water to natural streams or sewers.	1.0 ppm	This quantity will be rapidly oxidized to a near zero concentration rapidly

5. EVALUATION OF CURRENT AND NEAR FUTURE HYDRAZINE DISPOSAL PROCESSES

Hydrazine is generally destroyed by oxidation to water and nitrogen. In dilute solution, dissolved oxygen, catalysis, or bacterial action convert hydrazine to nitrogen, hydrogen, ammonia and water. Therefore, there are no problems in dealing with the products from waste treatment. Current disposal practices for hydrazine are briefly described in the following paragraphs together with recommendations as to adequacy.

Option Number 1--Open Pit Burning

Hydrazine poured into an open lined pit is burned to nitrogen and water. The transfer of the hydrazine and the ignition must be accomplished by a remote means.[1300] For drum quantities of hydrazine this method is generally acceptable.

Option Number 2--Incineration

The Air Force has a minimum of ten trailer mounted incinerators capable of incinerating up to 6 GPM of hydrazine in a variety of mixtures with water (from 100 percent hydrazine to 100 percent water). The effluents from the units is limited to 0.03 lbs/min NO_x when incinerating hydrazine.[1994] These units are acceptable for disposing of large quantities of hydrazine.

Option Number 3--Catalytic Decomposition

One of the applications for hydrazine in its use as a monopropellant. When hydrazine is passed over a support (usually aluminum oxide) coated with certain metals or metal oxides, it is decomposed into nitrogen, hydrogen and ammonia. The details of catalyst composition are usually found in the classified literature. In most cases the catalyst is expensive, but TRW Systems has preliminary data on a low cost catalyst that should be further investigated.

Option Number 4--Diluting With Water and Holding

If Hydrazine is diluted with water, e.g., after spills, and placed in open lined ponds or holding tanks, the hydrazine is decomposed to water, nitrogen and ammonia by air oxidation and bacterial action.[1300] For small quantities of hydrazine in aqueous solution this method is acceptable if adequate space is available.

Option Number 5--Chemical Treatment

Small quantities and dilute solutions are collected in open containers and treated with oxidizing compounds such as 10 percent hydrogen peroxide or calcium hypochlorite. The oxidizing agents should be applied slowly until in excess.[1300] This method is not recommended except for small quantities because considerable heat is liberated during decomposition.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Hydrazine does not appear to be a candidate for National Disposal Sites. It is anticipated that packaged hydrazine and hydrazine in aqueous waste streams will continue to be treated at the source of waste generation. The products of combustion or decomposition are the elements, water, or ammonia which do not present a secondary disposal problem.

7. REFERENCES

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1994. Coen Company. Liquid wastes. Chemical Engineering, 78 (14): 43, June 21, 1971, Advertisement.

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Hydrazine

IUC Name Hydrazine

Common Names Diamine

Structural Formula

N_2H_4

Molecular Wt. 32.05 Melting Pt. 1.5 Boiling Pt. 113.5

Density (Condensed) 1.008 g cc @ 20 C Density (gas) 1.1 @ 0 C

Vapor Pressure (recommended 55 C and 20 C)

0.07 psia @ 40 F 0.36psia @ 80 F 2.9psia @ 160 F

Flash Point 52. C Autoignition Temp. 270 C

Flammability Limits in Air (wt %) Lower 4.7% Upper 100% at 100 C

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Miscible Hot Water Miscible Ethanol Miscible

Others: acetone - miscible

Acid, Base Properties $N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$ $K = 8.5 \times 10^{-7}$

Highly Reactive with Acids, metal oxides

Compatible with Stainless steel, aluminum

Shipped in Bottles, drums, tank cars

ICC Classification Corrosive Liquid, White Label Coast Guard Classification White Label Corrosive Liquid

Comments

References (1) 1300

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PROFILE REPORT

Hydrocyanic Acid and Hydrogen Cyanide (215, 218)

1. GENERAL

Hydrogen cyanide (also known as hydrocyanic acid) is a water-white liquid at temperatures below 26.5 C. It has a faint odor of bitter almonds. Hydrogen cyanide is miscible in all proportions with water and alcohol, and in aqueous solution is weakly acidic; dissociation constant at 18 C is 1.3 x 10^{-9}. When not stabilized, hydrogen cyanide polymerizes spontaneously with explosive violence. Hydrogen cyanide is manufactured commercially by six different processes: (1) by treating a cyanide, usually sodium or calcium, with dilute sulfuric acid; (2) by catalytically reacting ammonia and air with methane or natural gas; (3) by recovery from coke oven gases; (4) decomposition of formamide; (5) from ammonia and hydrocarbons by electrofluid reaction in the presence of a platinum-rhodium catalyst; and (6) by pyrolytic decomposition of residues from beet-sugar molasses. The principal uses of hydrogen cyanide are in the manufacture of acrylonitrile, acrylates, adiponitrile, cyanide salts, dyes, fumigants, chelates, rubbers, and plastics.[1433]

The physical/chemical properties for hydrogen cyanide are summarized in the attached worksheet.

2. TOXICOLOGY

Human Toxicity

Hydrogen cyanide and the cyanides are true protoplasmic poisons, combining in the tissues with the enzymes associated with cellular oxidation. They thereby render the oxygen unavailable to the tissues, and cause death through asphyxia. The suspension of tissue oxidation lasts only while the cyanide is present; upon its removal, normal function is restored provided death has not already occurred. Hydrogen cyanide does not combine easily with hemoglobin but does combine easily with methemoglobin to form cyanmethemoglobin. Exposure to concentrations of 100 to 200 ppm for periods of 30 to 60 min can cause death. The TLV, American Conference of Governmental Industrial Hygienists (ACGIH) (recommended) is 10 ppm in air (11 mg per cubic meter). Hydrocyanic acid can be absorbed through the skin.[536]

Other Toxicity

Cyanides, either as hydrogen cyanide or its salts, are important industrial chemicals, and because of their solubility in water are often found in industrial aqueous waste streams. At low pH values, cyanide, as hydrocyanic acid, is especially toxic. Cyanide ion is, for the most part, unaffected by the basic water treatment plant. Many lower animals and fish are able to convert cyanide to thiocyanate ion, which does not inhibit respiratory enzyme activity. Hence, a permissible criterion has been recommended of 0.20 mg/l for waste discharged into streams, and a desirable criterion of complete absence from public waters was recommended by the Federal Water Pollution Control Administration (FWPCA) Water Quality Committee.[536]

3. OTHER HAZARDS

When hydrogen cyanide is exposed to heat, flame or oxidizing chemicals, a fire or explosion may occur. Under certain conditions, particularly contact with alkaline materials, hydrogen cyanide can polymerize or decompose explosively. The compressed gas is commonly stabilized by addition of acids.[1416]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Shipping

Liquid hydrogen cyanide is subject to DOT regulations for the transportation of explosives and other dangerous articles. It is defined a Class "A" poison. The commercial product usually contains 96 percent to 98 percent hydrogen cyanide with the balance water and small quantities of free mineral acids (about 0.05 percent) for stabilizing purposes.

When hydrogen cyanide is stored in bulk, steel storage tanks are used that should be kept cool and protected from mechanical injury. Routine inspection for stability (liquid colorless) should be carried out. Before filling with hydrogen cyanide, containers should be cleaned and treated to remove alkaline contaminants.

Hydrogen cyanide is packed for interstate shipment in metal cylinders, which must have not more than 125-lb water capacity and must be charged with not more than 0.6 lb of liquid for 1-lb water capacity of the cylinder. Before shipment, the cylinder must be tested to insure against leakage. This is done by passing a piece of paper treated with sodium picrate over the closure to test for escape of hydrogen cyanide. The cylinder must carry a "Poison Gas" label. Shipment may be made by freight but is not accepted by Railway Express.[1433]

Disposal/Reuse

Hydrogen cyanide appears in both aqueous and gaseous waste streams from hydrogen cyanide manufacturing plants, acidified cyanide salt (plating shops, metal treating plants, etc.), organic chemical and plastic manufacturing, and fumigating operations. In addition, coal coking and degassification plants and oil refining operations produce hydrogen cyanide as one of the byproducts. Complete removal of hydrogen cyanide from the effluent is difficult. HCN passes into waste water in the course of the wet scrubbing processes used to remove the H_2S, NH_3 and phenol contaminants. Alkaline scrubbing usually converts most of the hydrogen cyanide to the alkaline cyanide salt. Hydrogen and the residual unstripped hydrogen cyanide, though sometimes vented, are usually sent to a furnace where they are used as a fuel.[1963] Taking this into consideration, it is obvious that maximum concentrations of hydrogen cyanide must be recommended for both gas and aqueous effluent streams released to the environment. The recommendations are as follows:

Containment and Environment	Maximum Concentration	Basis for Recommendation
HCN released to air outside the boundaries of the processing plant.	0.1 ppm	0.01 TLV
HCN released to air inside the boundaries of the processing plant.	10 ppm	TLV (ACGIH) recommended[536]
HCN released to streams and lakes.	0.20 mg/l	FWPCA Water Quality Committee Recommendation[536].

5. EVALUATION OF CURRENT DISPOSAL PROCESS

Hydrogen cyanide in aqueous streams is easily destroyed by first adjusting the pH to the 10 to 11 range and adding chlorine or hypochlorite which converts the cyanide to cyanate. Then the pH is then adjusted to the 8 to 9 range and further oxidizing agent converts the cyanate to carbon dioxide and ammonia. Other methods though not often used are available and are discussed in the combined profile report for the cyanide salts. In an alternate equally acceptable method, hydrogen cyanide is removed from aqueous solution by passing air through the solution. The venting of this air containing hydrogen cyanide is not recommended, but instead the contaminated air must be passed through an alkaline scrubber.

The destruction of hydrogen cyanide is usually accomplished by incineration which produces only carbon dioxide and nitrogen along with possibly some NO_x that can be stripped from the incinerator effluent with an alkaline scrubber,[1562] or reduced over a catalyst.

Air containing hydrogen cyanide, either as an effluent from a storage tank, process, or from stripping of an aqueous solution, is absorbed by passing the air through a sodium or potassium hydroxide scrubber which produces the cyanide salt. The salts obtained in this manner are recovered upon evaporation of the water.[1963]

The disposal processes described are equally acceptable. The selection of disposal processes are governed by the economics of destruction/recovery.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Hydrogen cyanide does not appear to be a candidate for National Disposal Sites. It is anticipated that aqueous and gaseous waste streams containing hydrogen cyanide will continue to be treated at the source of the waste generation.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Hydrogen Cyanide

IUC Name Hydrogen Cyanide

Common Names Hydrocyanic Acid, Prussic Acid

Structural Formula

HCN

Molecular Wt. 27.03 Melting Pt. -13.2 C Boiling Pt. 25.7 C

Density (Condensed) 0.688 @ 20 C Density (gas) 0.969 @ 31 C

Vapor Pressure (recommended 55 C and 20 C)

360 torr @ 7 C 658.7 torr @ 21.9 C @

Flash Point 0 F Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water miscible Hot Water miscible Ethanol miscible

Others: ether-miscible

Acid, Base Properties Acid, weak

Highly Reactive with must be stabilized with acids, reacts with bases

Compatible with most metals

Shipped in metal cylinders, 125-lb water capacity

ICC Classification Class "A" Poison Coast Guard Classification Class "A" Poison

Comments Critical temperature 183.5 C

References (1) 1433

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PROFILE REPORT

Mercuric Cyanide (254)

1. GENERAL

Mercuric cyanide is one of the most stable of the simple cyanides. It is formed as colorless or white tetragonal prisms. At 320 C it begins to decompose and over 400 C it is completely decomposed into mercury and cyanogen.

Mercuric cyanide is formed when any simple cyanide or ferrocyanide is heated with a mercuric salt or mercuric oxide.[1433]

$$2KCN + HgCl_2 \rightarrow Hg(CN)_2 + 2KCl$$

$$2KCN + HgO + H_2O \rightarrow Hg(CN)_2 + 2KOH$$

$$2K_2Fe(CN)_6 + 6HgO + 4H_2O + 1/2\ O_2 \rightarrow 6Hg(CN)_2 + 8KOH + Fe_2O_3$$

Mercuric cyanide is used as a substitute for mercuric chloride in medicine as an antiseptic. Since mercuric cyanide is not ionized, it is less irritating to the tissues and it does not precipitate proteins or corrode steel instruments as does the chloride. Dry distillation of mercuric cyanide is used in the laboratory for the preparation of dry cyanogen. Patents have been issued, though they are apparently not used, on the introduction of mercuric cyanide into engine fuels as an "antidetonant" or antiknock agent.[1433]

2. TOXICOLOGY

When heated to decomposition, or on contact with acid or acid fumes, mercuric cyanide emits highly toxic fumes of cyanide and mercury. The threshold exposure limit for mercury is 0.01 ppm (0.1 mg per cubic meter of air) American Conference of Governmental Industrial Hygienists (ACGIH); TLV is 10 ppm (11 mg per cubic meter) for cyanides. The toxicology for cyanides is documented in Profile Reports on Hydrocyanic Acid (215) and Hydrogen Cyanide (218). Mercury is a general protoplasmic poison. After absorption mercury circulates in the blood and is stored in the liver, kidneys, spleen and bone. In industrial poisoning, the chief effect is upon the central nervous system and upon the mouth and gums.[0766] Because mercury has been found concentrated in sea life, its discharge is avoided.

3. OTHER HAZARDS

When mercuric cyanide is reacted in aqueous solution with mercuric oxide or chloride, mercuric oxycyanide of varying composition is formed. The approximate composition of mercuric oxycyanide is $3Hg(CN)_2 \cdot HgO$. The mercuric oxycyanide is reacted with various acids to form such compounds as mercuric cyanide nitrate, formate, acetate, oxalate and benzoate. Mercuric oxycyanide in the dry form is known to explode when being transferred from one container to another. Therefore, care must be taken not to form mercuric oxycyanide when mercuric cyanide is being prepared.[1433]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Mercuric cyanide is classed by DOT as a Class B poison requiring a Poison label. It is shipped in amber glass bottles, wooden kegs and fiber drums.

As with other cyanides, the release of the cyanide ion from mercuric cyanide must be controlled. The permissible level of cyanide ion in an effluent stream is 0.2 mg/l with a desirable criterion of complete absence (Federal Water Pollution Control Administration (FWPCA)).[0536] A goal of complete absence of mercury from effluents is in effect since the recent reported mercury buildup in certain fish.

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

With the goal of no mercury in waste streams, two processes were recently described that can be used to destroy mercuric cyanide. These two processes appear equally acceptable and are described briefly in the following paragraphs.

Option No. 1 - Sodium Borohydride Reduction

After alkaline chlorination to destroy the cyanide ion, sodium borohydride is used to reduce mercury ions to the metal.[1145] This is accomplished by adjusting the pH to the 8 to 10 range and adding a solution of sodium borohydride which reduces mercury to the elemental form and liberates hydrogen. The liberated hydrogen is passed through dilute nitric acid to remove mercury vapors. The mercury is collected by filtering, and purified by vacuum distillation. Sodium borohydride cost is $13.00 per lb, but one lb reduces 21 lbs of mercury.[1145]

Option No. 2 - Ion Exchange Collection

After destruction of cyanide by chlorination, mercuric ions are collected on a special ion exchange resin, Q-13 sold by Aktiebolaget Billingsfors-Langed of Billingsfors, Sweden. This resin lowers mercury concentration to the 100 ppb level. Then an absorption tower packed with Q-sorb, sold by the same company as Q-13, reduces the mercury content to a few parts per billion. The Q-13 resin can be regenerated to recover the mercury, but the Q-sorb resin cannot be regenerated which causes a storage/ disposal problem that was not discussed.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Mercuric cyanide wastes are candidates for disposal at National Disposal Sites since the goal of no mercury in waste streams requires their collection wastes. It would be expected that concentrated wastes could be treated commercially as described earlier and remarketed, but mixed wastes would require treatment and storage or burial.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Mercuric Cyanide

IUC Name Mercuric Cyanide

Common Names

Structural Formula

$Hg(CN)_2$

Molecular Wt. 252.65 Melting Pt. 320 C decomposes Boiling Pt.

Density (Condensed) 4.00 g/cc @ 20 C Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 9.3g/100ml at 14 C Hot Water 53g/100ml at 100 C Ethanol soluble

Others: pyridine, acetone, ammonia

Acid, Base Properties

Highly Reactive with mercuric oxide or chloride

Compatible with most materials of construction

Shipped in amber glass, bottles, wooden kegs, and fiber drums

ICC Classification Class "B" Poison Coast Guard Classification Class "B" Poison

Comments

References (1) 1433

PROFILE REPORT

meta and *para*-Nitrochlorobenzene (302)

1. GENERAL

Nitrochlorobenzene (*meta* and *para*) are yellow crystals having melting points of 46 C and 82 C, respectively.[1492] Both materials are highly toxic and have similar effects on the body. Their effects are analogous to those of nitrobenzene.[766]

Mononitrochlorobenzenes can be obtained from benzene by a combination of nitration and halogenation. The order of the operations determines the positional isomer content of the product. *meta*-Nitrochlorobenzene is obtained by nitration of benzene followed by chlorination. By reversing the order, a mixture results containing about two parts of the *para* isomer to one of the *ortho*. On a technical scale, fairly sharp separation of the isomers resulting from nitration is made by freezing out the bulk of the higher-melting *para* compound, fractionating the liquid portion, and further freezing.[1655]

Domestic production of *p*-nitrochlorobenzene was reported as over 88.9 million pounds for the year of 1970.[1718] Production figures are not available for the *meta* compound. Manufacturers of the *meta* compound are E. I. du Pont de Nemours and Company Incorporated[1718] and Universal Oil Products.[1718] The *para* compound is manufactured by American Aniline Products,[1718] E. I. du Pont de Nemours Company Incorporated,[1718] Monsanto Company,[1718] and Universal Oil Products.[1718]

2. TOXICOLOGY[766]

Intoxication from these materials can be serious. When absorbed, they form methenoglobin and give rise to cyanosis and blood changes. Their effects are analogous to those of nitrobenzene (Profile Report on nitrobenzene). They can cause poisoning by the pulmonary route and their effects are cumulative. The toxic hazard rating for ingestion and inhalation is high for both materials.

3. OTHER HAZARDS

In industry it is the dust of these materials that is most often the source of intoxication.[766] Protective goggles, gloves and breathing masks capable of removing airborne dust should be worn when working with these materials in the open. There is only a moderate fire hazard associated with the nitrochlorobenzenes.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Gloves and chemical goggles should be worn to protect the hands and eyes when handling nitrochlorobenzene flakes or crystals. A breathing mask capable of eliminating nitrochlorobenzene dust is recommended when handling these materials in other than fume hoods or closed systems.

The nitrochlorobenzenes (meta and para) are shipped as crystals and flakes according to Insterstate Commerce Commission regulations.[278] They are classed as Poison B and require a poison label on all packages.

These materials should be stored in tightly closed containers away from heat or flame. When heated to decomposition, they emit highly toxic fumes of oxides of nitrogen and phosgene.[766] They can also react with oxidizing materials.

Disposal/Reuse

A definition of acceptable criteria for the disposal of meta and para-nitrochlorobenzenes must also take into account acceptable criteria for the release of hydrogen chloride, hydrochloric acid, and nitrogen oxides to the environment, since current practice in nitrochlorobenzene disposal involves some processes that reduce nitrochlorobenzene to these materials.[1432]

Current disposal techniques utilize incineration and land burial. These methods are acceptable provided the recommended maximum concentration of nitrochlorobenzene, hydrogen chloride, hydrochloric acid and nitrogen oxides in effluent streams released to the environment are not exceeded. The recommended maximum concentrations are as follows:

Contaminant and Environment	Maximum Concentration and Point Source Release Rate	Basis of Recommendation
p-Nitrochlorobenzene released to the atmosphere	0.01 mg/M^3/24 hr.	0.01 TLV
m-Nitrochlorobenzene released to the atmosphere	(Not available)	
Hydrogen chloride released to the atmosphere	0.05 ppm (0.07 mg/M^3)/24 hr.	0.01 TLV
Hydrochloric acid released to the atmosphere	0.05 ppm (0.07 mg/M^3)/24 hr.	0.01 TLV
Nitrogen oxides released to the atmosphere	0.05 ppm (0.07 mg/M^3)/24 hr.	0.01 TLV

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

The nitrochlorobenzenes are expected to appear primarily as dilute organic waste streams and to a much lesser degree as dilute aqueous waste and concentrated waste. The processing options are briefly described in the following paragraph together with recommendations as to their adequacy.

In the event it becomes necessary to dispose of a significant quantity of concentrated nitrochlorobenze, two adequate disposal options are available. The first option is to incinerate the material using scrubbers to remove the hydrogen chloride and nitrogen oxides from the effluent gas streams. The second option is to bury the material in a qualified landfill. It is recommended that dilute organic waste be disposed of in the same manner. Incineration is the recommended method of disposing of dilute aqueous waste.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The nitrochlorobenzenes are expected to appear primarily as dilute organic waste and to a much lesser degree as dilute aqueous waste and concentrated waste. It is anticipated that facilities for handling the disposal of these wastes will be located at the manufacturing sites. These compounds are not judged to be candidates for National Disposal Sites.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET 302

H. M. Name m-nitrochlorobenzene

IUC Name 1-chloro-3-nitrobenzene[1]

Common Names m-chloronitrobenzene[2]

Structural Formula

$C_6H_4ClNO_2$[1]

Molecular Wt.[1] 157.56 Melting Pt.[1] 44 C Boiling Pt. 235-6 C[1]

Density (Condensed) 1.534 @ 20/4 C[2] Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ____ @ ____ ____ @ ____

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water Insoluble[1] Hot Water ____ Ethanol Slightly soluble[1]

Others: Soluble in ether[1] benzene[1] CS_2[1] chloroform[1] acetic acid[1]

Acid, Base Properties ____

Highly Reactive with Can react with oxidizing materials[2]

Compatible with Glass, metals, earthenware[3]

Shipped in ____

ICC Classification Poison B[3] Coast Guard Classification ____

Comments Mfg. by:[4] E. I. du Pont de Nemours and Company Incorporated; Universal Oil Products

References (1) 1570 (4) 1718
(2) 766
(3) 278

Give a reference for each entry.

Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET 302

H. M. Name p-nitrochlorobenzene

IUC Name 1-chloro-4-nitrobenzene[1]

Common Names p-chloronitrobenzene[2]

Structural Formula

$C_6H_4ClNO_2$[1]

Molecular Wt.[1] 157.56 Melting Pt.[1] 83 C Boiling Pt.[1] 242 C

Density (Condensed) 1.520 Density (gas)

Vapor Pressure (recommended 55 C and 20 C)

Flash Point 127 C[2] Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insoluble[1] Hot Water Ethanol Slightly soluble[1]

Others: Soluble in ether[1], CS_2[1]

Acid, Base Properties

Highly Reactive with

Compatible with Glass, metals, earthenware[3]

Shipped in

ICC Classification Poison B[3] Coast Guard Classification

Comments Mfg. by:[4] American Aniline Products Incorporated; Monsanto Company.

References (1) 1570 (4) 1718
(2) 766
(3) 278

Give a reference for each entry.

Supply units where necessary

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PROFILE REPORT

Nitrogen Mustards (306)

1. GENERAL

The nitrogen mustards are chemical warfare agents stored by Germany during World War II but never applied to a combat situation. 2,2',2" trichloro triethyl amine (HN-3) can be prepared using a chlorinating agent such as thionyl chloride together with 2,2',2'' trihydroxy triethyl amine hydrochloride and reacting the product with a strong base. 2,2' dichloro diethyl methyl amine (HN-2), and 2,2' dichlorotriethyl amine (HN-1) can be prepared by analagous techniques. The nitrogen mustards and their derivative have aquired considerable peacetime importance due to their use for cancer therapy.

2. TOXICITY[0778]

The nitrogen mustards are contact, inhalation, and eye poisons. The salts,particularly the hydrochlorides,can be used for poisoning water, foodstuffs and condiments and thus provide intoxication via the gastrointestinal tract. The liquid (as an aerosol) causes skin damage in concentrations above 0.001 mg/cm^2 of skin surface. The inhalation of nitrogen mustards causes severe respiratory difficulties. Concentrations of aerosol of 0.002 mg/l for 15 to 20 minutes leads to incapacity while concentrations of 0.25 to 1.0 mg/l have a lethal effect after brief exposure, 5 min. Slight eye damage occurs with concentrations as low as low as 0.0007 mg/l for a 15 min exposure. The lethal dose for man is between 10 and 20 mg per kilogram of body weight.

3. OTHER HAZARDS

The low vapor pressure of these compounds limits the possible flammability and explosive hazards. Combustion of the nitrogen mustards results in the formation of the pollutants hydrogen chloride and nitrogen oxides.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Due to their toxicity the nitrogen mustards require very careful handling, protective clothing, and masks. Materials contacted by these compounds must be decontaminated actively since nitrogen mustards are slow to hydrolyze due to low solubility. A 5 percent hydrochloric or sulfuric acid solution is sufficient to form the salts which can then be washed away with large volumes of water. The water solution should be collected and dried to recover the highly toxic salts. Dry calcium hypochlorite reacts readily with the nitrogen mustards and their salts to form nonpoisonous products. This reaction, when concentrated nitrogen mustards are involved, is so violent as to cause ignition and fire hazard.

Storage and Transportation

The nitrogen mustards can be stored for considerable periods in glass or steel containers if an inhibitor such as thiourea is present. The salts of the nitrogen mustards can be stored indefinitely.

No direct information on the transportation of nitrogen mustards was uncovered; however, sealed vans might be used for greater than laboratory quantities.

Disposal/Reuse

The recovery of nitrogen mustards in large quantities for military or non-military purposes is not practical due to the limited stability of the material.

The recommended levels for nitrogen mustard in air, water and soil have not yet been derived.

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Dilute Wastes

Option No. 1 - Separation. The nitrogen mustards have slight solubility pH values equal to or higher than 7. Thus, liquid phase separation equipment such as the centrifuge could be used for the recovery of the mustards from alkaline water media. If the nitrogen mustards have dissolved, because of an acid environment, the addition of base to neutrality or slight alkalinity will cause phase separation. The separated concentrated nitrogen mustard can be treated as described below. The effluent clarified water should for safety be treated with acidified hypochlorite solution.

Concentrated Wastes

Option No. 1 - Incineration. (Transportable Disposal System). The transportable Disposal System which is described in the Profile Report on the Organophosphorus Nerve Agents can be applied to munitions or tanks containing the nitrogen mustards in concentrated form. The combustion products of the nitrogen mustards are carbon dioxide, water and nitrogen oxides. The nitrogen oxides require scrubbing or reduction to nitrogen and oxygen before the combustion gases are released to the atmosphere.

Option No. 2 - Chemical Reaction. The nitrogen mustards, when acidulated, react with calcium hypochlorite in solution to yield compounds with a much lower toxicity including aldehydes, chloramines, and chlorates. The reactions are violent with dry or highly concentrated hypochlorite. Care must be taken to ensure that sufficient agitation and time is allowed for the reaction due to the phase separation problem.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The hazard to man associated with vesicants such as the nitrogen mustards requires their disposal at National Disposal Sites when present in munitions or when there are large quantities of the materials. The recommended techniques are summarized below:

Process	Order of Preference	Remarks
Incineration (Transportable Disposal System)	First Choice	The TDS is designed for materials of this type and is adequately safeguarded.
Chemical Reaction	Second Choice	The reaction with hypochlorite appears adequate for smaller quantities.

REFERENCES

0778. Franke, S., Manual of military chemistry. Chemistry of Chemical Warfare Agents. v. 1. Washington, Office, Assistant Chief of Staff for Intelligence, Headquarters, Department of The Army, 1968. 375 p.

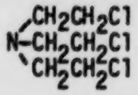
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 306

IUC Name 2,2" dichloro diethyl amino 2 cnloro ethane

Common Names HN-3, Nitrogen Mustard

Structural Formula



$N(CH_2CH_2Cl)_3$

Molecular Wt.[1]

Melting Pt.[2] -4 C

Boiling Pt. 230-235 C

Density (Condensed) 1.24 @ 20 C

Density (gas) 7 @
Air =1.00

Vapor Pressure (recommended 55 C and 20 C)

.0069 mm Hg @ 20 C

.009 mm Hg @ 0 C

@

Flash Point °

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.16 g/l

Hot Water

Ethanol

Others: halogenated alkanes, propane, benzene, carbon disulfide, sulfur mustard, chloropicrin

Acid, Base Properties slightly basic

Highly Reactive with

Compatible with iron and steel

Shipped in

ICC Classification

Coast Guard Classification

Comments Colorless and odorless, oily liquid, decomposes on heating. Thiourea used to stabilize (prevent demerization).

References (1) 0778
(2)
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

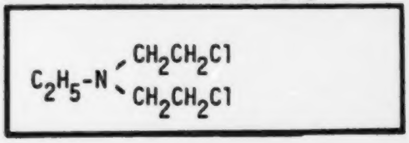
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 306

IUC Name 2,2" dichloro diethyl amino 2 chloro ethane

Common Names Nitrogen Mustard HN-1

Structural Formula



$$C_2H_5-N\begin{matrix} \diagup CH_2CH_2Cl \\ \diagdown CH_2CH_2Cl \end{matrix}$$

Molecular Wt.[1] ______ Melting Pt.[2] -34.4 C Boiling Pt. ______

Density (Condensed) 1.0861 @ 4 C Density (gas) ______ @ ______ ______

Vapor Pressure (recommended 55 C and 20 C)

12 mm Hg @ 85.5 C ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water ______ Hot Water ______ Ethanol ______

Others: ______

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in ______

ICC Classification ______ Coast Guard Classification ______

Comments ______

References (1) 0778
(2)
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

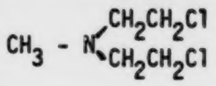
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 306

IUC Name 2' chloro ethyl methyl amino 2 chloro ethane

Common Names Nitrogen Mustard, HN-2

Structural Formula



$$CH_3 - N\begin{matrix} CH_2CH_2Cl \\ CH_2CH_2Cl \end{matrix}$$

Molecular Wt.[1] Melting Pt.[2] -65 C Boiling Pt.

Density (Condensed) 1.13 @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

9 mm Hg @ 71 C @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 0778

(2)

(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

PROFILE REPORT

Sodium Azide (378)

1. GENERAL

Sodium azide, NaN_3, is a colorless crystalline substance described as being highly toxic.[0766]

Sodium azide is prepared from sodium amide and nitrogen monoxide according to the following reaction[1492]:

$$2NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$$

Fairmont Chemical Company in Newark, New Jersey is the only manufacturer of sodium azide in the United States. Last year they produced about 500,000 pounds of the chemical for domestic use.[2024]

Sodium azide is used mainly as a reactant in the production of lead, silver, antimony, and mercury azides. It also has a medical use in treating hypertensive encephalopathy and other conditions which demand immediate lowering of blood pressure (dose 0.2 to 4.0 micrograms/kg body weight/minute intravenous).[1492]

The sources of sodium azide wastes may include the following: (1) sodium azide manufacturers; (2) sodium azide wholesalers; (3) manufacturers that use sodium azide as a reactant in their production process. Mr. Patterson of DuPont, however, claims that in their process for making lead azide, sodium azide does not appear in the waste stream.[2025] This is because there is essentially a 100 per cent conversion of sodium azide to lead azide in the reaction process.

The physical and chemical properties of sodium azide are summarized in the attached worksheet.

2. TOXICOLOGY

The toxicity of sodium azide is due to the azide group (-NNN). Much of the knowledge of azide toxicity has been gained from industrial exposures and laboratory studies involving hydrazoic acid, HN_3. Dilute aqueous solutions and hydrazoic acid vapors from azide reactions have caused noticeable and measurable effects in industrial and laboratory workers.

Hydrazoic acid is easily adsorbed into the bloodstream after inhalation of the vapor or spray. The chief physiological effect is a marked lowering of the blood pressure with an accompanying rise in heart beat and an increase in the respiration rate. Eye and nose irritation, headache, weakness, and unsteadiness have also been reported following continued industrial exposures. Recovery from these effects is rapid and low level (less than 4 ppm) exposures which cause these symptoms do not appear to produce any permanent abnormal conditions.[2026]

The estimated oral LD_{50} value to the rat for sodium azide is 46 mg/kg of body weight.[1312] The 48-hour Median Tolerance Limit (TL_m) of sodium azide for bluegills is 980 micrograms/liter as established by the Federal Water Pollution Control Administration,[0536] and is indicative of the water pollution hazard associated with sodium azide.

3. OTHER HAZARDS

The explosive hazard of sodium azide is moderate when shocked or exposed to heat. However, the explosiveness of sodium azide increases somewhat when it is contaminated with certain materials. When heated to decomposition, sodium azide emits toxic fumes of nitrogen oxides.[0766]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Care should be exercised in handling sodium azide because of the high toxicity and explosive nature of the compound. The use of leather gloves, a heavy face shield, and a laboratory coat is recommended in handling the material. It is advisable to work behind a barricade (body shield or wall). Avoid unnecessary heat, friction or impact.[0095]

Sodium azide should be stored in a warehouse in metal containers.[2024] It should be stored away from foodstuffs, feeds, or any other material intended for human or animal consumption.

Sodium azide must be transported in wooden boxes with inside containers which are securely closed paper bags, placed within a waterproof duplex bag. The net weight of material in one outside box should not be over 100 pounds.[0278] There must be a poison B label on every box.

Disposal/Reuse

Fairmont Chemical Company has a policy of accepting excess amounts of sodium azide and contaminated sodium azide for reprocessing.[2024]

In the laboratory, small quantities of waste azide solutions can be discharged into the sink if adequate cold water dilution is provided. Under these circumstances, the safe disposal of sodium azide is defined in terms of the recommended maximum concentration of the contaminant in water:[2026]

Contaminant in Water	Maximum Concentration	Basis for Recommendation
Sodium Azide	9.8 micrograms/liter	.01 TL_m for fish

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Concentrated Wastes

Option #1 - Reprocessing/Disposal. Fairmont Chemical Company, the only major producer of sodium azide in the United States, has indicated its willingness to accept excessive or waste sodium azide for reprocessing, purification or disposal. The details of the reprocessing technique were not revealed. Fairmont Chemical's method for disposal of sodium azide is to react it with sulfuric acid solution and sodium nitrate in a hard rubber or teflon vessel.[1236] Nitrogen dioxide is generated by this reaction and the gas is run through a scrubber before it is released to the atmosphere. It is conceivable that any industry that handles sodium azide in significant amounts would probably have facilities for reacting the sodium azide and treating the evolved nitrogen dioxide gas.

Option #2 - Incineration. The complete and controlled oxidation of sodium azide in air or oxygen with adequate scrubbing and ash disposal is possible if the sodium azide is mixed with other combustible wastes. Since the combustion process produces nitrogen and sodium oxides, an adequate gas clean-up system must be installed to alleviate the air pollution problem.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Considering the small production and consumption of sodium azide, as well as provisions for return of waste sodium azide to the producer, it is felt that sodium azide does not warrant National Disposal Site treatment. The high cost of sodium azide is in itself an incentive to the manufacturers that use the compound to minimize the amount of waste material. The simple method of disposing of sodium azide by reaction with sulfuric acid and sodium nitrate can easily be performed by any firm that handles the compound. In summary, processes for the exclusive treatment of sodium azide are not recommended for inclusion in the National Disposal Site scheme.

7. REFERENCES

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2025. Personal communication. Mr. Patterson, DuPont Chemical Company to D. DalPorto, TRW Systems, June 19, 1972. Aqueous sodium azide waste treatment.

2026. Safety in handling hazardous chemicals. Los Angeles, Matheson, Coleman and Bell, 1969. 24 p.

HAZARDOUS WASTES PROPERTIES WORKSHEET

#378

H. M. Name Sodium Azide

IUC Name

Common Names Sodium Azide

Structural Formula

NaN_3

Molecular Wt.[1] 65.02 Melting Pt.[2] decomposes Boiling Pt. decomposes in a vacuum

Density (Condensed) 1.846 @ 20 Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 41.7g/100cc @ 17 C Hot Water Ethanol 0.314/100cc @ 16 C

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B Coast Guard Classification Poison B

Comments Shock will explode it; when heated to decomposition, it emits toxic fumes of nitrogen oxides, and may explode.

References (1) 0766
(2)
(3)

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[1] Give a reference for each entry.

[2] Supply units where necessary

PROFILE REPORT

Tetraethyl- and Tetramethyllead (425,427)

1. GENERAL

Tetraethyllead (TEL) and tetramethyllead (TML) are colorless, oily liquids of very high toxicity. Individually and in mixtures they constitute the major gasoline antiknock agents now in use. More stringent exhaust emission standards are expected to reduce their predominance as gasoline additives.[1506] They are commonly believed to be the major source of environmental lead pollution and they are likely to interfere with the operation of the automobile antipollution equipment that will be necessary to meet future exhaust emission requirements.

Although many synthetic schemes for the preparation of TEL and TML have been disclosed in the technical and patent literature, there are only two basic processes in domestic, commercial use.[1433] By far the more important of the two involves the reaction of sodium-lead alloy with ethyl or methyl chloride as shown in Equation 1. Upon completion of the reaction, the TEL or TML is steam distilled to remove it from the other products. The organolead compounds are then purified by washing with dilute solutions of oxidizing agents (e.g., hydrogen peroxide, sodium dichromate) and then with water. After purification, the TEL and TML are usually mixed with the other ingredients that make up the antiknock fluid and with an identifying dye. The compounded fluid is then pumped into tank cars or bulk-storage tanks. This process, in several modifications, is used by Du Pont (Antioch, Calif. and Deepwater, N.J.), Ethyl Corporation (Baton Rouge, La. and Houston, Texas) and Houston Chemical (Beaumont, Texas) with a combined capacity (1971) of 790 million pounds per year.[1506]

$$1\ NaPb + 4\ C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 3\ Pb + 4\ NaCl \qquad (1)$$

Nalco Chemical (Freeport, Texas) uses an electrolytic process for TML, based on the electrolysis of a solution of methylmagnesium chloride and excess methyl chloride in an ether solvent, with lead metal acting as the anode.[1433] The overall electrolytic reaction is shown in Equation 2. The capacity of the Nalco plant is 40 million pounds per year.[1506]

$$2\ CH_3MgCl + CH_3Cl + Pb \rightarrow (CH_3)_4Pb + 2\ MgCl_2 \qquad (2)$$

TEL and TML are also available for use in antiknock fluids as mixtures of organolead compounds produced by a redistribution reaction of mixtures of TEL and TML in the presence of Lewis-acid catalysts (Equation 3).[1433] The production capacity for the redistributed mixtures is included in the total 830 million pound per year capacity cited above.[1506]

$$Me_4Pb + Et_4Pb \rightarrow Me_4Pb + Me_3EtPb + Me_2Et_2Pb + MeEt_3Pb + Et_4Pb \qquad (3)$$

The only nonantiknock use for TEL and TML of commercial importance is in the preparation of organomercury fungacides,[1433] another group of materials under investigation as a possible environmental danger.

The physical/chemical properties of TEL and TML are summarized in the attached worksheets.

2. TOXICOLOGY[0766, 1433]

Tetraethyl- and tetramethyllead are extremely toxic materials. Acute or chronic poisoning may result from ingestion, inhalation or absorption through skin. Overexposure to TEL or TML severely affects the central nervous system. The initial symptoms are weakness, nervousness, severe constipation and colic-like pains. Heavy or prolonged exposure may result in death.

The American Conference of Government and Industrial Hygienists has recommended a threshold limit value for TEL and TML of 0.075 mg/M^3 of air.

3. OTHER HAZARDS

Tetraethyl- and tetramethyllead are considered to be fire hazards when exposed to heat and flame.[0766] The hazardous nature of a fire involving these materials is substantially increased by the danger of exposure to the toxic fumes of TEL, TML, and their decomposition products.

These organolead compounds are also known to react exothermically with halogens, mineral acids and oxidizing agents.[1433]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation and Personnel Safety with Tetraethyl- and Tetramethyllead

The most significant potential for exposure to TEL and TML occurs in the manufacture of the compounds and their blending into gasoline at the refinery.[1433] Subsequent to the blending operation at the refinery, exposure to these materials is limited by the low concentration in gasoline (less than 4 ml/gal) and the normal methods of handling the fuel at service stations.

In the manufacturing and blending operations emphasis has been placed on eliminating vapor, dust and liquid leaks.[1433] Adequate exhaust ventilation must be provided in all work areas to maintain the concentration of TEL and TML vapors well below the recommended TLV of 0.075 mg/M^3 of air.[0766] Personnel likely to contact these materials in concentrated form should be provided with proper protective gloves and be made thoroughly cognizant of the danger they pose.

Regular medical examinations should be an integral part of a program to guard against the danger of lead intoxication.[1433] The medical examination should include a urine or, preferably, a blood test to monitor the level of lead in the worker's body. The mean normal lead concentration in whole blood is said to be 0.03 mg/100 cc and in urine a concentration of 0.03 mg of lead per liter is considered normal.[1433]

TEL and TML are generally stored and shipped in steel vessels. Accidental spills which occur in handling or transport can be decontaminated by reaction of the lead compound with dilute potassium permanganate or bromine solution.[1433]

Both of these tetraalkyllead compounds are classified by the ICC, Coast Guard and IATA as Poison B, requiring a poison label. The IATA does not permit their shipment on passenger flights and limits cargo flights to a maximum of 220 liters.[0766]

Disposal/Reuse of Tetraethyl- and Tetramethyllead

The recovery and reuse of lead and lead compounds is an integral part of the manufacture of TEL and TML.[1433] Only 25 percent of the lead in the NaPb alloy (see Equation 1) is utilized on each pass through the process. It is a matter of economic necessity that the excess lead be recovered, purified and returned to the process.

Tetraethyl- and tetramethyllead wastes are most likely to appear as dilute aqueous solutions generated in their manufacture,[1046] and as components of the sludge and scale which collect in plant and refinery storage and mixing facilities.[1788]

The adequate treatment of the waste requires that the hazards involved in handling these toxic materials be reduced, that their concentration in effluent aqueous streams be at acceptable levels (<1 ppm[1787]), and that the lead-containing compounds removed from the wastes be converted to forms suitable for reuse. All of those requirements can be met by the conversion of the organic lead compounds to inorganic lead compounds. The inorganic materials can be more easily removed from solution and reduced to metallic lead in a smelting operation. Other advantages of the organic to inorganic conversion accrue by virtue of lessened volatility and reduction of the high lipoid solubility of the organic materials (responsible for their ease of absorption through the skin).[0766]

The recommended maximum concentration of tetraethyl- and tetramethyllead released to the environment from tetralkyllead disposal processes are as follows:

Concentration and Environment	Maximum Concentration and Point Source Release Rate	Basis of Recommendation
TEL or TML released to the atmosphere	0.75 $\mu g/M^3/24$ hrs.	0.01 TLV

5. EVALUATION OF CURRENT AND NEAR FUTURE TETRAETHYL- AND TETRAMETHYLLEAD DISPOSAL PROCESSES

The processes currently employed for the disposal of tetraalkyllead wastes are all basically the same, differing only in detail as dictated by the location and nature of the waste generation source.

Current Disposal Processes

Dilute, aqueous solutions of organic lead compounds generated in the manufacturing process are the major type of TEL and TML wastes. The contaminated water is produced during steam distillation, washing, purification and maintenance operations.[1046] The aqueous wastes are collected in settling pits to recover lead and insoluble lead salts.[0534] The water from the settling pits is then treated to adjust its pH to 8 to 9.5 in the presence of precipitating agents such as ferrous sulfate or sodium carbonate.[0534, 1046] Precipitated lead salts are recovered for recycling to lead metal,[1786, 1787] and the water is allowed to return to the environment.

Despite the ubiquity of the disposal method described above, it is now generally agreed that it does not reduce the lead concentration in effluent streams to acceptable levels. In view of the inadequacy of the current disposal process, the DuPont plant in Antioch, California has been forced to store its lead-containing wastes pending the completion of an incineration facility to convert them to a form more amenable to recycle by lead smelters.[1787] The problem of lead recycling is especially complicated at the Antioch plant, which uses a continuous rather than batch TEL synthesis.[1787]

The Baton Rouge plant of the Ethyl Corp. has also experienced difficulty in maintaining acceptably low lead effluent concentrations.[1786] They are pursuing conventional (unspecified) methods of reducing those concentrations.

The scale and sludge which form in TEL and TML storage, mixing and transport vessels are another source of tetraalkyllead waste. The former practice of dumping the old tanks containing lead residues at sea is no longer used.[1787, 1788] The lead sludges are buried or sold to secondary smelters for recycle.[1788] Petroleum refineries follow the practice of exposing the sludges to the air (weathering) until they are "inactive," after which they are landfilled.[1788] Presumably, the weathering process results in the slow oxidation of the lead compounds to insoluble PbO. However, it seems likely that the evaporation of toxic organic lead compounds cannot be avoided in this essentially uncontrolled exposure and that this method may result in local atmosphereic organic lead pollution.

Near Future Disposal Processes

The disposal processes outlined in the following subsections do not appear to be in actual use at this time. They are currently under development or have been reported in the literature.

Option No. 1 - Incineration. An incineration process to convert organic and inorganic lead wastes to PbO for recycle to lead metal is now under development.[1787] The use of this or a similar process for treatment of TEL and TML waste streams is recommended as the most desirable method of reducing their deleterious effects on the environment. An acceptable lead waste burning installation must be fitted with efficient scrubbing devices to prevent the contamination of stack effluents with toxic lead or lead-containing particulates and/or vapors.

Option No. 2 - Ion Exchange. Strongly acidic cation exchange resins have been shown to effect almost complete removal of organic lead compounds from typical TEL aqueous waste streams.[1046] The inorganic lead compounds were removed by conventional means before the stream was introduced to the ion exchange column and the final concentration of lead in the effluent water was less than 1 ppm. After elution from the column with caustic soda the eluate was subjected to oxidative chlorination, affording almost complete conversion to recoverable inorganic lead compounds. Although a judgment with respect to economic practicality of this process is not possible with the data in hand, the removal of organic lead compounds from TEL wastes with ion exchange resins appears to be technically attractive. A complete disposal system incorporating this process must also provide for rendering the inorganic lead obtained suitable for conversion to metallic lead.

Option No. 3 - Improved Precipitation Methods. A number of methods designed to improve the removal of lead-containing compounds from TEL and TML aqueous wastes are now under study.[1787] One such method involves the treatment of aqueous effluents from tetraalkyllead manufacture by: (1) adjusting the pH of the effluent to between 8.0 to 9.5; (2) intimately contacting the aqueous effluent with an ozone-containing gas in the presence of a soluble carbonate; (3) precipitating the converted inorganic lead compounds; and (4) separating the precipitated compounds.[0534] Reduction of the dissolved organic lead content to below 5 ppm is claimed.[0534] Any improved precipitation should be coupled to a process for conversion of the precipitated lead compounds to metallic lead for reuse.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Aqueous tetraethyl- and tetramethyllead waste streams do not appear to be candidates for disposal at National Disposal Sites. The aqueous, organolead wastes are generated at six manufacturing facilities belonging to relatively large, sophisticated chemical firms. Although these wastes are not now being treated in a completely acceptable manner, the problems are under intensive study and appear to be amenable to solution by the application of existing technology.

The lead-containing sludges and scales formed in TEL and TML storage, transportation and mixing vessels present a more complicated problem. Their sources are both more numerous and more diverse than those of the aqueous wastes, ranging in size and sophistication from major oil refineries to local, owner-operated service stations. Many of these purveyors of tetraalkyllead-containing gasolines will be unable to dispose of sludge and scale wastes in an acceptable manner. Therefore, the lead-containing sludges and scales may represent a class of materials that could be profitably sent to National Disposal Sites for treatment by incineration and subsequent recycle to metallic lead.

Another, perhaps controlling factor that must be considered with regard to the applicability of tetraalkyllead wastes to National Disposal Sites is the probable diminishing use of these compounds as gasoline additives.[1506] A governmental decision to ban the use of the lead antiknock compounds in gasoline may render the question of the disposal of their wastes academic.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET #427

H. M. Name Tetramethyllead

IUC Name Tetramethyllead

Common Names Lead tetramethyl, TML

Structural Formula

$(CH_3)_4Pb$

Molecular Wt. 267.33 Melting Pt.[1] -27.5 C Boiling Pt.[1] 110 C

Density (Condensed)[2] 1.9952 @ 20 C/4 C Density (gas)[3] 9.2 @

Vapor Pressure[2] (recommended 55 C and 20 C)

22.5 mm @ 20 C 116.6 mm @ 55 C @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility[1]

Cold Water Insoluble Hot Water Ethanol sl. sol.

Others: benzene, ether, gasoline

Acid, Base Properties

Highly Reactive with Oxidizing agents;[3] acids and halogens[2]

Compatible with

Shipped in Steel

ICC Classification[3] Poison B Coast Guard Classification[3] Poison B

Comments Sources[4]: DuPont, Nalco Chemical, Ethyl Corp.

References (1) 1570 (4) 1718
(2) 1433
(3) 0766

Give a reference for each entry.

Supply units where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET #425

H. M. Name Tetraethyllead

IUC Name Tetraethyllead

Common Names Lead tetraethyl, TEL

Structural Formula

$(CH_3CH_2)_4Pb$

Molecular Wt. 323.44 Melting Pt.[1] -136.8 C Boiling Pt.[1] 200 C (d)

Density (Condensed)[2] 1.6528 @ 20 C/4 C Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

0.47 mm @ 20 C[2] 2.5 mm @ 55 C[2] 19 mm @ 91 C[1]

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility [1]

Cold Water Insoluble Hot Water ____ Ethanol sl. sol.

Others: Benzene, ether, gasoline

Acid, Base Properties ____

Highly Reactive with Oxidizing agents;(3) acids and halogens(2)

Compatible with ____

Shipped in Steel

ICC Classification[3] Poison B Coast Guard Classification Poison B

Comments Begins to decompose at or above 100 C[2]

Sources:[4] DuPont, Houston Chemical Corp., Nalco Chemical, Ethyl Corp.

References (1) 1570 (4) 1718
(2) 1433
(3) 0766

Give a reference for each entry.

Supply units where necessary